Problems in Physical Chemistry

K K SHARMA

PROBLEMS IN PHYSICAL CHEMISTRY

BY THE SAME AUTHOR

A Textbook of Physical Chemistry (*Co-author*)
Problems in Organic Chemistry (*Co-author*)
An Introduction to Practical Chemistry (*Co-author*)

PROBLEMS IN PHYSICAL CHEMISTRY

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PREFACE TO THE SECOND EDITION

The second edition is the result of the substantial rewriting of many chapters of the book. Several new problems have been added in each chapter. This has been done to meet the needs of students of different educational background with different professional fields in mind. Both CGS and the SI units have been employed throughout.

Suggestions to improve the book will be gratefully acknowledged.

K. K. SHARMA

PREFACE TO THE FIRST EDITION

In the study of Physical Chemistry, one comes across a large number of mathematical concepts that are introduced from time to time. Such concepts can better be clarified by solving numerical problems. This book is intended to help the student of physical chemistry clarify his concepts, by solving problems, which cannot be satisfactorily done in the textbook, due to the paucity of space. Each chapter begins with a brief introduction to the topic, laying special emphasis on mathematical relationship and units of the physical quantities. A large number of problems have been solved to illustrate the subject. This is then followed by exercises with the answers given at the end. Hints have also been given, wherever necessary.

Although SI units have been used very frequently, some non-SI units have also been retained because of their practical importance or use in the specialized fields.

The chapter on the mathematical methods apprises the student of the usage of slide rule and logarithmic tables.

This book, though meant primarily for B.Sc. pass and honours students of the Indian universities, will also be useful for engineering, pharmacy students, and those preparing for the competitive examinations.

The author is grateful to Dr Dillip Singh Sharma, Lecturer in Chemistry, for his timely help and valuable suggestions.

Suggestions for the improvement of this book are welcome.

K. K. SHARMA

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1

MOLES, FORMULAS AND STOICHIOMETRY

The term stoichiometry, refers to relationships between quantities of reactants and products in chemical systems. The weight of each element present in a sample of a compound may be determined by analytical procedures. It is common to express this weight in terms of per cent. This is known as percentage composition.

$$\text{Percentage composition} = \frac{\text{Mass of element in sample}}{\text{Total mass of sample}} \times 100$$

Formulas, tell us the relative number of different atoms making up a chemical compound. One of the most important quantitative concepts in chemistry is the mole. Since individual atoms or molecules are so small as to be virtually impossible to work with, the idea of a large collection of atoms or molecules, namely, the "mole" was developed. A mole of atoms is the mass in grams equal to the atomic weight. The mole is defined as the number of carbon atoms in 12.00 grams of the isotope $^{12}C_6$. This number is known as Avogadro's number and has a value 6.023×10^{23}. This is a huge number!

The atomic weights listed in the periodic table, gives the mass of an atom of an element, as it occurs in nature relative to that of ^{12}C atom, which is taken to be exactly 12. Atomic weights are average values. Often they are not whole numbers because most natural elements consist of more than one isotope. Carbon, for example, is mostly $^{12}C_6$ but contains small amounts of $^{13}C_6$ and $^{14}C_6$, so the average atomic weight of carbon is 12.0115. The atomic weight of hydrogen is 1.00797; of cobalt 58.9332, and so on. The gram atomic weight is the mass of an element in grams, which is numerically equal to its atomic weight.

Molecular weight may be determined by summing atomic weights when the formula of a molecular substance is known. For instance, we know that the formula of water is H_2O. This tells us that each water molecule contains two hydrogen atoms and one oxygen atom. One mole of water molecules would, therefore, contain two moles of hydrogen atoms and one mole of oxygen atoms. Therefore, the molecular weight of water is $(2\times1.009)+(1\times16.00)=18.02$ g. The gram molecular weight of water is 18.02 g. Formula weight is a widely used term as it can be employed both for molecular and ionic substances.

Empirical formula is the relative number of each kind of atom in a molecule.

Molecular formula is the total number of each kind of atom in a molecule.

A chemical equation represents a chemical reaction. The reactants are written on the left side and the products on the right side of the equation. A balanced equation gives (*i*) reactants and products in a chemical reaction, (*ii*) relationship between moles and masses of products and reactants in a chemical reaction. For balancing more complicated equations, the concept of oxidation numbers of the elements must be understood. Oxidation numbers ure assigned according to the following arbitrary rules:

(*a*) All the elements in their elemental state are assigned zero oxidation number.

(*b*) Oxygen in compounds is assigned an oxidation number of—2.

(*c*) Hydrogen in compounds is assigned an oxidation number of +1.

(*d*) The sum of the oxidation numbers for a molecule must equal zero.

(*e*) The sum of the oxidation numbers for an ionic species is equal to the charge on the ion.

Rules for balancing simple equations. The following rules must be followed for balancing equations:

1. Balance the metals present first.
2. Balance the non-metals except hydrogen and oxygen.
3. Balance hydrogen and oxygen.
4. Check all elements.
5. Repeat in the same order till all are balanced.

Sometimes redox equations which occur in the absence of a solvent may be quite difficult to balance by inspection method. When several substances are involved, the key ratio required to balance the equation may be readily apparent. In such cases oxidation number method may be employed. The following rules must be followed:

1. Determine the oxidation number of each element present

$$\overset{(0)}{\mathrm{Al}} + \overset{(0)}{\mathrm{S}} \longrightarrow \overset{(+3)}{\mathrm{Al}_2}\overset{(-2)}{\mathrm{S}_3}$$

2. Indicate the changes in oxidation number.

$$\begin{array}{c} \text{oxidation} \\ \overline{\downarrow \quad \text{increase}+3/\text{atom} \quad \downarrow} \\ \text{Al}+\text{S} \quad \rightarrow \quad \text{Al}_2\text{S}_3 \\ \underline{\uparrow \quad \text{decrease}-2/\text{atom} \quad \uparrow} \\ \text{reduction} \end{array}$$

3. Multiply the substances oxidised and reduced by the proper coefficients to make the increase in oxidation number equal to the decrease.

$$\begin{array}{l} \text{increase } 2\times 3=6 \\ \text{decrease } 3\times 2=6 \\ 2\,\text{Al}+3\text{S}\rightarrow \text{Al}_2\text{S}_3 \end{array}$$

4. Continue as for simple equations.
5. Check.

Problem 1.1. Balance the equation:

$$\text{Ba}+\text{NH}_3\rightarrow \text{Ba}_3\text{N}_2+\text{H}_2$$

Rule 1.

$$\begin{array}{llll} (0) & (-3)(+1) & (+2)(-3) & (0) \\ \text{Ba} & +\text{NH}_3 \longrightarrow & \text{Ba}_3\ \text{N}_2 + & \text{H}_2 \end{array}$$

Rule 2.

$$\begin{array}{c} \text{oxidation} \\ \overline{\downarrow \text{increase}+2/\text{atom} \downarrow} \\ \text{Ba}+\text{NH}_3 \quad \longrightarrow \quad \text{Ba}_3\text{N}_2+\text{H}_2 \\ \underline{\uparrow \text{decrease}-1/\text{atom} \uparrow} \\ \text{reduction} \end{array}$$

Rule 3.

$$3\text{Ba}+2\text{NH}_3\rightarrow \text{Ba}_3\text{N}_2+3\text{H}_2$$

Problem 1.2. Using the modern experimental techniques, the mass of one atom can be determined. If the mass of one sodium atom has been found to be 3.82×10^{-23}g, how many sodium atoms are contained in one mole of sodium?

Solution. The atomic weight of sodium is 22.9 g, and 3.82×10^{-23} g is the weight of one atom of sodium. 22.9 g will be the weight of $\frac{22.9}{3.82\times 10^{23}}$ or the number of sodium atoms in one gram-atom $=6.02\times 10^{23}$. A mole of atoms is the mass in grams equal to the atomic weight. A mole of atoms contains Avogadro's number of atoms (6.02×10^{23}).

Problem 1.3. Calculate the per cent yield if the reaction of 64.0 g of NaBH_4 with iodine produced 15.0 g of BI_3.

Solution. 1. Balanced equation

$$\text{NaBH}_4+4\text{I}_2\longrightarrow \text{BI}_3+\text{NaI}+4\text{HI}$$

2. 1 mole $NaBH_4 \longrightarrow 1$ mole BI_3

$$\begin{array}{lrl} NaBH_4 & 1\times 23.0 = & 23.0 \\ & 1\times 10.8 = & 10.8 \\ & 4\times 1.0 = & \underline{4.0} \\ & & 37.8 \text{ g/mole} \\ BI_3 & 1\times 10.8 = & 10.8 \\ & 3\times 126.9 = & \underline{380.7} \\ & & 391.5 \text{ g/mole} \end{array}$$

$\frac{64.0}{37.8} = 1.69$ mole $NaBH_4$

Calculated yield $= 1.69$ mole $NaBH_4 \times 392 = 662$ g BI_3

3. Per cent yield $= \frac{15.0}{662} \times 100 = 2.27$ per cent.

Problem 1.4. In a specific compound, the per cent of oxygen is 18.6. There is one mole of oxygen atom (a gram-atom) in each mole of the compound. What is the molecular weight of the compound?

Solution. 100 g compound contains 18.6 g oxygen and 81.4 g other atoms.

18.6 g oxygen corresponds to 81.4 g of other atoms

16 g oxygen will correspond to $\frac{81.4}{18.6}\times 16.0$

$= 70$ g of other atoms

$\therefore$ Molecular weight $= 70+16 = 86.$

or

18.6 g of oxygen corresponds to 100 g of compound.

16.0 g of oxygen will correspond to $\frac{100}{18.6}\times 16.0 = 86.$

Problem 1.5. A sample of sodium chloride, NaCl contaminated with KBr weighs 0.225 gram. It was found to contain 0.840 gram of sodium.

(*i*) How many moles of Na did the sample contain?
(*ii*) How many moles of NaCl did the sample contain?
(*iii*) How many moles of Cl did the sample contain?
(*iv*) How many grams of NaCl did the sample contain?
(*v*) What was the purity of the sample?

Solution. (*i*) $\frac{0.0840}{23.0 \text{ g/mole}} = 3.65\times 10^{-3}$ mole Na

(*ii*) $\frac{3.65\times 10^{-3} \text{ mole Na}}{1 \text{ mole Na}} = 3.65\times 10^{-3}$ mole NaCl (*iii*) $\dfrac{3.65\times10^{-3}\ \text{NaCl}}{1\ \text{mole Na}\times1\ \text{mole NaCl}}=3.65\times10^{-3}\ \text{mole Cl}$

(*iv*) $\dfrac{3.65\times10^{-3}\ \text{mole NaCl}}{58.5\ \text{g NaCl}}=0.214\ \text{g NaCl}$

(*v*) $\dfrac{0.214\ \text{g NaCl}\times100}{0.225}=95.1$ per cent.

Problem 1.6. Cyclopropane is a gas that is used as a general anesthetic. The gas has a density of 1.50 g/litre at 50°C and 0.948 atm. (*a*) What is the molecular weight of cyclopropane? (*b*) The empirical formula of cyclopropane is CH_2. What is the molecular formula of the compound?

Solution. (*a*) Since the density is 1.50 g/litre, 1.50 g of the gas will occupy 1.00 litre under the conditions specified.

$$PV=\left(\frac{g}{M}\right)RT$$

$$(0.948\ \text{atm})(1.00\ \text{litre})=\left(\frac{1.50\ \text{g}}{M}\right)(0.082\ \text{litre atm/K. mol})\ (323\ \text{K})$$

$\therefore\ M=42.0$ g/mol

(*b*) The formula weight of the empirical formula is 14.

Since (Empirical formula)$_n$=molecular weight.

$$\therefore\quad n=\frac{42}{14}=3$$

∴ The molecular formula of propane will be C_3H_6.

Problem 1.7. How many litres of CO(g) at STP are needed to reduce 1.00 kg of Fe_2O_3(s)? The chemical equation is

$$Fe_2O_3(s)+3CO(g)\longrightarrow 2Fe(s)+3CO_2(g)$$

Solution. From the chemical equation

1 mol Fe_2O_3 = 3 mol CO
1 mol Fe_2O_3 = 159.6 g Fe_2O_3
1 mol CO = 22.4 litres CO at STP

$$\therefore\ ?\ \text{litre CO}=1000\ \text{g}\ Fe_2O_3\left(\frac{1\ \text{mol}\ F_2O_3}{159.6\ \text{g}\ FeO_3}\right)\left(\frac{3\ \text{mol CO}}{1\ \text{mol}\ Fe_2O_3}\right)\left(\frac{22.4\ \text{litres CO}}{1\ \text{mol CO}}\right)$$

$$=421\ \text{litres CO.}$$

Problem 1.8. A 0.400 g sample of sodium azide, NaN_3(s), is heated and decomposes.

$$2NaN_3(s)\longrightarrow 2Na(s)+3N_2(g)$$

What value of $N_2(g)$, measured at 25°C and 0.980 atm is obtained?

Solution. From the chemical equation:

$$2 \text{ mol } NaN_3 = 3 \text{ mol } N_2$$
$$1 \text{ mol } NaN_3 = 65.0 \text{ g } NaN_3$$
$$\therefore \ ? \text{ mol } N_2 = 0.400 \text{ g } NaN_3 \left(\frac{1 \text{ mol } NaN_3}{65.0 \text{ g } NaN_3}\right)\left(\frac{3 \text{ mol } N_2}{2 \text{ mol } NaN_3}\right)$$
$$= 0.00923 \text{ mol } N_2$$

We find the volume of N_2 (g) by using the equation of state.

$$PV = nRT$$
$$(0.980 \text{ atm})(V) = (0.00923 \text{ mol})(0.821 \text{ litre/K. mol})(298 \text{ K})$$
$$V = 0.230 \text{ litre.}$$

Problem 1.9. Morphine contains 67.3 per cent carbon, 4.6 per cent nitrogen and remaining are other constituents. Calculate the relative number of carbon and nitrogen atoms in morphine.

Solution. 100 grams of morphine contains 67.3 g carbon and 4.6 g nitrogen. The atomic weight of carbon is 12.011 g/gram-atom and that of nitrogen is 14.006 g/gram-atom.

$$67.3 \text{ g of carbon} = \frac{67.3}{12.011} = 5.60 \text{ gram-atoms}$$

$$4.3 \text{ g of nitrogen} = \frac{4.3}{14.006} = 0.33 \text{ gram-atom.}$$

5.60 gram-atoms of carbon per 0.33 gram-atom of nitrogen is the same as 5.60 atoms of carbon per 0.33 atom of nitrogen or C = 17 atoms N = 1 atom.

Problem 1.10. Natural oxygen consists 99.759 per cent of ^{16}O with mass 15.9949 amu, 0.037 per cent of ^{17}O with mass 16.991 amu and 0.204 per cent of ^{18}O with mass 17.9991 amu. With this distribution, calculate the chemical atomic weight of natural oxygen.

Solution. Let the total number of atoms = 100,000 of these

99,759 will have mass 15.9949 amu =	1,595,635
37 will have mass 16.9991 amu =	630
204 will have mass 17.9991 amu =	3,670
100,000 atoms will weigh =	1,599,935

The average atomic weight of natural oxygen will be 15.999.

Problem 1.11. A drop of water is about 0.05 ml. The density of water at room temperature is about 1.0 g/ml. How many H_2O molecules are present in a drop of water?

Solution. Volume of 1 drop of H_2O = 0.05 ml

Weight of 1 drop of H_2O = $0.05 \times (1.0 \text{ g/ml})$

= 0.05 g

The molecular weight of $H_2O = 2\times1+1\times16 = 18.0$ amu.
Since one gram mole of water at NTP contains 6.02×10^{23}

$$18 \text{ g } H_2O \text{ contains} = 6.02\times10^{23} \text{ molecules}$$

$$0.05 \text{ g } H_2O \text{ contains} = \frac{6.02\times10^{23}\times0.05}{18}$$

$$= 2\times10^{21} \text{ molecules.}$$

∴ Number of water molecules in a drop of water = 2×10^{21}.

Problem 1.12. Green plants produce glucose ($C_6H_{12}O_6$) and molecular oxygen by "photosynthesis" of carbon dioxide and water. How many grams of CO_2 are required to produce one mole of glucose?

Solution. The chemical reaction in photosynthesis can be symbolized as,

$$6CO_2+6H_2O\rightarrow C_6H_{12}O_6+6O_2$$

$$\text{Number of gram of } CO_2 = 1 \text{ mol } C_6H_{12}O_6 \times \frac{6 \text{ moles } CO_2}{1 \text{ mole } C_6H_{12}O_6}$$

$$\frac{44.0 \text{ g } CO_2}{1 \text{ mole } CO_2}$$

$$= 264 \text{ g } CO_2$$

$$= 264 \text{ g } CO_2.$$

Problem 1.13. The percentage composition of a compound was found to be 65.8 per cent Pb, 16.5 per cent Cr and 17.7 per cent O. What is the empirical formula of the compound? (Atomic weights of Pb=207.2, Cr=52.0, O=16)

Solution. Let us consider 100 grams of compound.

$$\text{Number of moles of Pb} = \frac{65.8}{207.2}$$

$$= 0.318 \text{ mole.}$$

$$\text{Number of moles of Cr} = \frac{16.5}{52.0}$$

$$= 0.317 \text{ mole.}$$

$$\text{Number of moles of O} = \frac{17.7}{16.0}$$

$$= 1.11 \text{ moles.}$$

$$\frac{0.317 \text{ mole Cr}}{0.318 \text{ mole Pb}} = 1 \text{ (2 Cr for 2 Pb)}$$

$$\frac{1.11 \text{ mole O}}{0.318 \text{ molePb}} = 3.5 \text{ (7.0 for 2 Pb)}$$

The empirical formula is $Pb_2Cr_2O_7$.

Problem 1.14. How many grams H_2 must react with an excess of O_2 to produce 5.40 g H_2O?

Solution. There are several new features in this problem:

(*i*) O_2 is in excess.

(*ii*) Information is sought about the required amount of one of the reactants (H_2) instead of the product (H_2O).

(*iii*) Information is given and sought in the unit gram rather than mole.

$$\therefore \text{Number of grams of } H_2 = 5.40\text{g } H_2O \times \frac{1 \text{ mole } H_2O}{18.0 \text{ g } H_2O} \times \frac{2 \text{ mole } H_2}{2 \text{ mole } H_2O} \times \frac{2.02 \text{ g } H_2}{2 \text{ mole } H_2}$$

$$= 0.606 \text{ g } H_2.$$

Problem 1.15. Hydrazine, N_2H_4 (used as a fuel in rocket systems) can be produced according to the following reaction:

$$ClNH_2 + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl$$

When 1.00 kg $ClNH_2$ is reacted with large excess of NH_3, 473 g N_2H_4 is produced. What is the per cent yield of the reaction?

Solution. For calculating the per cent yield both the theoretical and actual yield must be known:

Actual yield of hydrazine is 473 g.

Theoretical yield is the maximum amount of N_2H_4 that can be produced by reacting 1.00 kg $ClNH_2$ with an excess of NH_3. Number of gram of hydrazine,

$$N_2H_4 = 1.04 \text{ kg } ClNH_2 \times \frac{1000 \text{ g } ClNH_2}{1.0 \text{ kg } ClNH_2} \times \frac{1 \text{ mole } ClNH_2}{51.5 \text{ g } ClNH_2} \times \frac{1 \text{ mole } N_2H_4}{1 \text{ mole } ClNH_2} \times \frac{32.0 \text{ g } N_2H_4}{1 \text{ mole } N_2H_4}$$

$$= 621 \text{ g } N_2H_4.$$

$$\text{Per cent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

$$= \frac{437 \text{ g } N_2H_4}{621 \text{ g } N_2H_4} \times 100 = 70.4.$$

Problem 1.16. It was found that 25 cm^3 of $\frac{M}{10}$ phosphorus acid

(H_3PO_3) neutralised exactly 40 cm³ of a solution containing 5 g sodium hydroxide per dm³. Deduce the equation for the reaction, between sodium hydroxide and phosphorus acid.

Solution. Number of moles of $H_3PO_3 = \frac{25}{1000} \times \frac{1}{10} = 2.5 \times 10^{-3}$

Number of moles of $NaOH = \frac{40}{1000} \times \frac{5}{40} = 5 \times 10^{-3}$

∴ the mole ratio of the reactants is

$NaOH : H_3PO_3 = 5 \times 10^{-3} : 2.5 \times 10^{-3} = 2:1$

Hence the equation for the reaction is

$2NaOH + H_3PO_3 = Na_2HPO_3 + 2H_2O$

Problem 1.17. A small piece of pure aluminium metal having a volume of 0.650 cm³ is reacted with an excess of hydrochloric acid. What is the weight of hydrogen obtained? (The density of aluminium is 2.70 g/cm³)

Solution. Number of gram of aluminium $= 0.65 \times 2.70$

$= 1.76 \text{ g Al}$

Number of mole of aluminium $= \frac{1.76 \text{ g}}{27.0} = 0.0652 \text{ mole}$

Number of mole of Hydrogen $= \frac{0.0652 \times 3}{2} = 0.0978 \text{ mole}$

Number of grams of H_2 $= \frac{0.0978 \times 2.02 \text{ g } H_2}{1 \text{ mole } H_2}$

$= 0.198 \text{ g } H_2$

Problem 1.18. Calculate the oxidation number of the italicized element in the following compounds.

(*a*) H_2SO_4, (*b*) SO_2, (*c*) MnO_2, (*d*) $K_2Cr_2O_7$, (*e*) MnO_4^-, (*f*) $K_4Fe(CN)_6$

Solution. Let x be the oxidation number of the italicized element.

(*a*) H_2SO_4

$$1 \times 2 + x + (-2) \times 4 = 0$$
$$2 + x - 8 = 0$$
$$x = +6$$

(*b*) SO_2

$$x + (-2) \times 2 = 0$$
$$x = +4$$

(*c*) MnO_2

$$x+(-2)\times 2=0$$
$$x=4$$

(*d*) $K_2Cr_2O_7$

$$(+1)\times 2+2x+(-2)\times 7=0$$
$$2+2x-14=0$$
$$x=+6$$

(*e*) MnO_4^-

$$x+(-2)\times 4=-1$$
$$x-8=-1$$
$$x=+7$$

(*f*) $K_4Fe(CN)_6$

$$(+1)\times 4+x+(-1)\times 6=0$$
$$x=+2$$

Problem 1.19. Balance the following equations:

(*a*) $H_3AsO_4+H_2S\rightarrow H_3AsO_3+S+H_2O$

(*b*) $KMnO_4+FeCl_2+HCl\rightarrow KCl+H_2O+MnCl_2+FeCl_3$

(*c*) $Sn+HNO_3+H_2O\rightarrow H_{10}Sn_5O_{15}+NO$

Solution. (*a*) In this reaction the oxidation number of As changes from +5 to +3. The net change is 2. The oxidation number of S in H_2S is -2 and it becomes zero in element S. The net change is again 2. The equation is thus balanced.

(*b*) The oxidation number of Mn changes from +7 to +2 a change of 5. The oxidation number of Fe changes from +2 to +3 a change of 1. The balanced equation will be

$$KMnO_4+5FeCl_2+8HCl\rightarrow KCl+4H_2O+MnCl_2+5FeCl_3$$

(*c*) The oxidation number of Sn changes from 0 to +4 change of 4, i.e., change of 20 per molecule of $H_{10}Sn_5O_{15}$. The oxidation number of nitrogen changes from + 5 to + 2 a change of 3. The balanced equation will be

$$15Sn+20HNO_3+H_2O\rightarrow 3H_{10}Sn_5O_{15}+20NO$$

EXERCISES

1.1. How many moles are there in

(*a*) 17.5 g of Sn	(*c*) 7.20 g of H_2O
(*b*) 50.0 g of NaCl	(*d*) 160.0 g of CCl_4

[**Ans.** (*a*) 0.147, (*b*) 0.855, (*c*) 0.40, (*d*) 1.05.]

1.2. How many molecules are there in

(*a*) 6.0 moles of benzene	(*c*) 6.0 g of NaCl
(*b*) 6.0 g of benzene	(*d*) 6.0 g of XeF_4

[**Ans.** (*a*) 3.61×10^{24}, (*b*) 4.62×10^{22}, (*c*) There are no molecules of NaCl, (*d*) 1.74×10^{22}.]

1.3. Analysis of chlorophyll shows that it contains 2.68 per cent magnesium. How many atoms of magnesium does 1.00 g of chlorophyll contain?
[**Ans.** 6.62×10^{20} atoms.]

1.4. Natural bromine is composed only of $^{79}_{35}Br$ and $^{81}_{35}Br$. The first of these isotopes has a mass of 78.9183 amu and the second 80.9163 amu. Calculate the relative abundance of the two isotopes.
[**Ans.** 50.65 per cent $^{79}_{35}Br$ and 49.35 per cent $^{81}_{35}Br$.]

1.5. How many atoms of copper are there in a piece of copper that weighs the same as a piece of aluminium that contains 486×10^{21} aluminium atoms.
[**Ans.** 2.08×10^{22}.]

1.6. In making transistors one needs to control the concentration of impurity very carefully. Suppose you wanted to make a germanium transistor containing 1.0×10^{18} boron atoms per cubic centimetre as impurity. If the density of germanium is 5.35 g/cm^3, what relative weights of germanium need to be mixed.
[**Ans.** 5.35 g of germanium and 1.8×10^{-5} g of boron.]

1.7. LSD is a complex compound whose mass is made up of 74.27 per cent carbon, 7.79 per cent hydrogen, 12.99 per cent nitrogen and 4.95 per cent oxygen. What per cent of the atoms in LSD are carbon atoms?
[**Ans.** 40.8 per cent,]

1.8. Calculate the weight of one molecule of quinine, $C_{20}H_{24}N_2O_2$.
[**Ans.** 5.39×10^{-23}g.]

1.9. Iron metal reacts with chlorine gas according to the equation: $2Fe(s)+3Cl_2(g)\rightarrow2FeCl_3(g)$. How many moles of $Cl_2(g)$ are required to convert 3.6 mole Fe to $FeCl_3$?
[**Ans.** 5.4 mole Cl_2.]

1.10. The reaction of calcium hydride with water can be used to prepare small quantities of hydrogen gas.

$$CaH_2(s)+2H_2O(l)\rightarrow Ca(OH)_2(aq.)+2H_2(g),$$

(*a*) How many moles of $H_2(g)$ result from the reaction of 150 g CaH_2 with excess of water?

(*b*) How many grams H_2O are consumed in the reaction of the 150 g CaH_2?

[**Ans.** (*a*) 7.13 mole H_2; (*b*) 128 g H_2O.]

1.11. Pure silver metal results when silver carbonate is decomposed on heating, according to the reaction,

$$2Ag_2CO_3(s)\rightarrow4Ag(s)+2CO_2(g)+O_2(g)$$

In one particular reaction, 12.3 g Ag is obtained. How many grams of Ag_2CO_3 must have been decomposed?
[**Ans.** 15.7 g.]

1.12. A 12.0 g sample of an aluminium copper alloy consisting of 9.5 per cent Al is reacted with an excess of hydrochloric acid. Only the Al reacts. How many grams of H_2 are produced?
[**Ans.** 1.28 g H_2.]

1.13. How many millilitres of a water solution of $KMnO_4$ containing 158g/l must be used to complete the conversion of 75.0 g KI to iodine (I_2) by the reaction

$$2KMnO_4+10KI+8H_2SO_4\rightarrow6K_2SO_4+2MnSO_4+5I_2+8H_2O.$$

[**Ans.** 90.5 ml.]

1.14. A material *X* was found to contain 8.62×10^{21} molecules of *X* in 3.39g of *X*. Calculate the molecular weight of *X*.

1.15. A drug marijuana owes its activity to tetrahydrocannabinol, which contains 70 per cent as many carbon atoms as hydrygen atoms and 15 times as many hydrogen atoms as oxygen atoms. The number of moles in a gram of tetrahydrocannabinol is 0.00318. Determine its molecular formula. [Ans. $C_{21}H_{30}O_2$.]

1.16. An impure sample of aluminium sulphate weighs 2.732 grams. It was found to contain 7.75×10^{-3} moles of $Al_2(SO_4)_3$. What is the purity of the sample expressed in terms of percentage of aluminium sulphate? [Ans. 97.1 per cent.]

1.17. How many grams of hydrogen sulphide contain one half as many molecules of H_2S as there are in 100 grams of iron? [Ans. 30.6 g.]

1.18. Dichlorofluoromethane, a widely used refrigerant, can be prepared by the following reactions:

$$CH_4+Cl_2\rightarrow CCl_4+HCl$$
$$CCl_4+HF\rightarrow CCl_2F_2+HCl$$

How many moles of Cl_2 must be used to produce 25.0 moles of CCl_2F_2? [Ans. 1.0×10^2 mole Cl_2.]

1.19. Which of the following statements are true and which are false? Explain.

(*a*) A reaction tends to go to completion if it is carried out in an open beaker.

(*b*) All reactions in which a gaseous product forms go to completion.

(*c*) Continuous removal of one of the products of a chemical reaction causes the reaction to go to completion.

[Ans. (*a*) false; (*b*) false; (*c*) true.]

1.20. Which of the following reactions would you expect to go to completion and which to be reversible?

(*a*) $FeS(s)+HCl(aq)\rightarrow FeCl_2(aq)+H_2S(g)$

(*b*) $NO(g)+O_2(g)\rightarrow NO_2(g)$

(*c*) $Na_2SO_4(aq)+BaCl_2(aq)\rightarrow NaCl(aq)+BaSO_4(s)$

(*d*) $Cl_2(aq)+H_2O(l)\rightarrow HCl(aq)+HCl(aq)$

[Ans. (*a*) completion; (*b*) reversible; (*c*) completion; (*d*) reversible.]

1.21. What is the empirical formula of a compound for which an analysis gave 0.653 mole of K, 0.653 mole of Cl, and 1.306 mole of O. [Ans. $KClO_2$.]

1.22. The per cent of nitrogen in a compound is 20.0 per cent and there are 2.00 moles of nitrogen atoms per mole of compound. What is the molecular Weight of the compound? [Ans. 140 g/mole.]

1.23. An unknown oxide of manganese is reacted with carbon to form manganese metal and carbon dioxide. Exactly 31.6 g of the oxide Mn_xO_y, yield 13.2 g of CO_2. Find the simplest formula of the unknown oxide. [Ans. Mn_2O_3.]

1.24. Nitromethane, (CH_3NO_2) is used as a fuel in aircraft and in racing car engines. When burned the products are CO_2,H_2O and NO. How many grams of oxygen are required to completely burn 122 grams of CH_3NO_2? [Ans. 80.0 g.]

1.25. Reaction of xenon with excess fluorine, produced a mixture of three products, each containing Xe and F and weighing a total of 2.073 grams by weight. The mixture contained 20 per cent XeF_2, 60 per cent *A* and 20 per cent *B*. Product *B* contained 0.193 gram of fluorine. Identify *A* and *B* (Total Xe=1331 g). [**Ans.** $A=XeF_4$; $B=XeF_6$.]

1.26. Ethyl alcohol reacts with phosphorus tribromide according to the following equation,

$$3C_2H_5OH+PBr_3\rightarrow 3C_2H_5Br+H_3PO_3$$

How many grams of C_2H_5Br could be produced from 5.42 grams of PBr_3? [**Ans.** 6.54 g.]

1.27. Calculate the number of moles of oxalic acid ($H_2C_2O_4$) present in a solution, 10.00 ml of which requires 18.35 ml of a 0.04982 M solution of NaOH for neutralisation. What is the molarity of the acid?

[**Ans.** Moles of oxalic acid in the sample=4.57×10^{-4}, molarity of oxalicacid=4.57×10^{-2}.]

1.28. The equation

$$CaCO_3(s)\rightarrow CaO(s)+CO_2(g)$$

represents the thermal decomposition of calcium carbonate in which carbon dioxide is driven off. According to this reaction, how many grams of $CaCO_3$ must be decomposed to yield (*a*) 3.00 moles of CO_2, (*b*) 4.0 g of CO_2, (*c*) 1.00 moles of CaO.

[**Ans.** (*a*) 300 g $CaCO_3$, (*b*) 9.1 g $CaCO_3$, (*c*) 100 g $CaCO_3$.]

1.29. A 7.00 g sample containing a mixture of $CaCO_3$ and $NaHCO_3$ is heated causing the two compounds to decompose according to the following equations:

$$2NaHCO_3(s)\rightarrow Na_2CO_3(s)+H_2O(g)+CO_2(g)$$
$$CaCO_3(s)\rightarrow CaO(s)+CO_2(g).$$

If, after decomposition is complete, there remains 4.00 g of solid residue, how much of the original sample was $NaHCO_3$? [Ans. 1.04 g.]

1.30. Write the balanced redox equation for the following half reactions:

(*i*) $MnO_4^-+8H^++5e^-\rightarrow Mn^{2+}+4H_2O$
$2Cl^-\rightarrow Cl_2+2e^-$

(*ii*) $H^++e^-+HNO_2\rightarrow NO+H_2$
$2HI\rightarrow I_2+2H^++2e^-$

(*iii*) $F_2+2e^-\rightarrow 2F^-$
$Al\rightarrow Al^{3+}+3e^-$

[**Ans.** (*i*) $2MnO_4^-+16H^++10Cl^-\rightarrow 2Mn^{2+}+8H_2O+5Cl_2$
(*ii*) $2HNO_2+2HI\rightarrow 2NO+2H_2O+I_2$
(*iii*) $3F_2+2Al\rightarrow 6F^-+2Al^{3+}$.]

1.31. Supply the missing coefficients in the following ionic equations:

(*i*) $\text{—}\ Ce^{4}+H_2O_2\rightarrow \text{—}Ce^{3+}+O_2+2H^+$

(*ii*) $\text{—}\ S_4O_6^{2-}+\text{—}OH^-\rightarrow 3S_2O_3^{2-}+2SO_3^{2-}+3H_2O$

(*iii*) $\text{—}\ IO_3^-+5HSO_3^-+\text{—}H^+\rightarrow I_2+\text{—}HSO_4^-+H_2O$

(*iv*) $\text{—}\ MnO_4^-+5H_2O_2+6H^+\rightarrow \text{—}Mn^{2+}\text{—}H_2O+\text{—}O_2$

[**Ans.** (*i*) 2→2 (*ii*) 2, 6→ (*iii*) 2, 2→5 (*iv*) 2→2, 8, 5.]

1.32. A mixture of the substances, $Ca(H_2PO_4)_2$, H_3PO_4, and $CaSO_4$, in the mole proportions represented in the equation given is called superphosphate of lime and is used as fertiliser.

$$5Ca_3(PO_4)_2+11H_2SO_4\rightarrow 4Ca(H_2PO_4)_2+2H_3PO_4+11CaSO_4$$

(*i*) How much H_2SO_4 is required to convert 2.00×10^3 kg $Ca_3(PO_4)_2$ tc superphosphate of lime?

(*ii*) How much superphosphate of lime can be obtained from 2.00×10^3kg of $Ca_3(PO_4)_2$ by this reaction?

(*iii*) Show that the total mass of products is equal to the total mass of reactants for the reaction described here.

[Ans (*i*) 1.39×10^3 kg H_2SO_4 (*ii*) 3.39×10^3 kg.]

2

GASEOUS STATE

Matter may exist in any of the three states of aggregation, solid, liquid and gas. The gaseous state is characterized by the fact that the density of matter in this state is lowest *i.e* the molecules in a gas are separated by a large distance.

Gas Laws

A gas that obeys Boyle's law and Charles' law is said to be ideal.

Boyle's law. Boyle found that at constant temperature the volume of gas appeared to vary inversely with pressure. Mathematically,

$$V \propto \frac{1}{P}$$

or

$$V=k\left(\frac{1}{P}\right) \qquad \ldots (1)$$

where k is a proportionality constant.

Charles' law. It states that volume for any definite quantity of a gas at constant pressure is directly proportional to the absolute temperature. Mathematically,

$$V=K_pT \qquad \ldots (2)$$

where K_p is a constant of proportionality, depends upon the pressure mass and nature of the gas and the units in which volume is expressed.

The combined gas law. If a quantity is independently proportional to two other quantities, a rule of proportionality states that the first quantity is also proportional to the product of the other two, *i.e.*

$$V \propto \frac{1}{P} \qquad \ldots (3)$$

$$V \propto T \qquad \ldots (4)$$

$$\therefore \quad V \propto \frac{T}{P}$$

or

$$PV=KT \qquad \ldots (5)$$

where K is constant of proportionality. This is known as the combined gas law. Since the volume of a gas is an extensive property, at constant temperature and pressure, the volume of an ideal gas is proportional to the number of moles of the gas. Since pressure and temperature are intensive properties, i.e., they do not depend on the number of moles of the gas, K must also be proportional to the number of moles of the gas. That is

$$K \propto n$$

or

$$K = Rn \qquad \ldots (6)$$

where R is a constant known as ideal gas constant.

Equation (5) can be written as,

$$PV = nRT \qquad \ldots (7)$$

Values for Ideal Gas Constant R

8.31431	$JK^{-1}\ mol^{-1}$
1.98717	cal $K^{-1}\ mol^{-1}$
0.0820575	l-atm $K^{-1}\ mol^{-1}$
8.31431×10^7	erg $K^{-1}\ mol^{-1}$

Graham's law. The rate of diffusion of a gas is inversely proportional to the square root of the molecular weight of the gas

$$\text{Rate} \propto 1/\sqrt{\text{Molecular weight}} \qquad \ldots (8)$$

Kinetic Theory of Gases

The kinetic theory of gases assumes model gas and we can postulate certain properties characteristic of a model gas.

First postulate. The gaseous substances consist of molecules that are far apart in comparison with their own diameters.

Second postulate. The gas molecules are in a state of constant random motion interrupted only by collisions with each other and with the walls of the container.

Third postulate. The gas molecules are perfectly elastic and the walls of the container are perfectly elastic.

Fourth postulate. The average kinetic energy of molecules is proportional to temperature.

From the kinetic theory of gases the pressure p exerted by an ideal gas can be calculated from the eapression,

$$p = \frac{1}{3}\frac{mn\overline{C}^2}{V} \qquad \ldots (9)$$

where m is the mass of one molecule, n is the number of molecules and $\overline{C}$ is the root mean square velocity. V is the volume occupied by the gas.

Average velocity. The average velocity C_{av} of the molecules may be defined as

$$C_{av} = \sqrt{\frac{8RT}{\pi M}} \qquad \ldots (10)$$

Most probable velocity. This is the velocity possessed by most of the molecules and is defined as

$$C \text{ (most probable)} = \sqrt{\frac{2RT}{M}} \qquad \ldots (11)$$

Root mean square velocity. The root mean square velocity $\bar{C}$ is defined as

$$\bar{C} = \sqrt{\frac{3RT}{M}} \qquad \ldots (12)$$

Boltzmann equation. It is a very important equation and finds applications in many aspects of physical chemistry. The equation is

$$\frac{n_2}{n_1} = e^{-E/RT} \qquad \ldots (13)$$

where n_1 is the number of molecules in any specified energy state 1, and n_2 is the number in the same volume in a state 2 in which the potential energy is E per mole in excess of that in state 1. Both states must be at the same temperature T. The exponential factor $e^{-E/RT}$ is known as Boltzmann factor.

Virial equation. It is given by the relation,

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots\ldots. \qquad \ldots (14)$$

where V is the molar volume, B and C depend on temperature but not on V.

Mean free path. The mean free path length L is defined as

$$L = \frac{1}{\sqrt{2}\,\pi\sigma n^*} \qquad \ldots (15)$$

where σ is the collision diameter. n^* is the number of molecules per cubic centimetre.

The number of collisions per second is known as collision number and is denoted by Z_1

$$Z_1 = \sqrt{2}\pi\sigma^2\bar{C}_{av}n^* \qquad \ldots (16)$$

$\bar{C}_{av}$ is the average molecular speed of molecules.

The number of collisions per second per cubic centimetre is called collision number and is denoted by Z_{11}. Since there are n^* molecules per cubic centimetre and each of these molecules has Z_1 collisions per second, the total number of collisions per second per cubic centimetre will be $\frac{1}{2}n^*Z_1$. The factor ensures that each collision will not be counted twice

$$Z_{11} = \frac{1}{2}\sqrt{2}\pi\sigma^2\bar{C}_{av}(n^*)^2$$

$$= \frac{1}{\sqrt{2}}\pi\sigma^2\bar{C}_{av}(n^*)^2 \qquad \ldots (17)$$

van der Waals equation. This equation is used to express the behaviour of real gases, and can be expressed as,

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT \qquad \ldots (18)$$

The constants a and b are known as van der Waal's constants and express the mutual attraction of molecules and their size respectively.

Critical constants. Consider a volatile liquid confined to a sealed container capable of withstanding very high pressures. As the temperature of the system is increased the density of the vapour will increase due to the increased number of molecules in the vapour phase. At the same time the volume of liquid will increase and so the density of the liquid will decrease. As the temperature is further increased a point will be reached at which the density of the vapour phase will equal that of the liquid phase. The temperature, pressure, and volume at which this occurs is called the critical temperature T_c, critical pressure P_c, and the critical volume, V_c, of the substance, and the point which they characterize is called the critical point of the substance. The critical constants are expressed in terms of van der Waal's constants, a and b, gas constant R, and the temperature of the gas *i.e.*

$$\left.\begin{array}{r} V_c = 3b;\ P_c = \dfrac{a}{27b^2} \\ T_c = \dfrac{8a}{27Rb} \end{array}\right\} \qquad \ldots (19)$$

Law of corresponding states. It can be shown that if the pressure, volume and temperature of a gas are expressed as fraction of critical pressure, critical volume, and critical temperature, the quantities thus obtained are known as reduced pressure π, reduced volume ϕ and reduced temperature θ *i.e.*

$$\pi = \frac{P}{P_c};\ \phi = \frac{V}{V_c};\ \theta = \frac{T}{T_c} \qquad \ldots (20)$$

On substituting these quantities in the van der Waals equation we get reduced equation of state,

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi-1) = 8\theta \qquad \ldots (21)$$

Problem 2.1. What volume would 1.3 moles of a perfect gas occupy at 39°C and 3.9 atm. pressurs?

Solution.

$$PV = nRT$$

$$\therefore \quad V = \frac{nRT}{P}$$

$$n = 1.3 \text{ mole}$$

$T=312$ K

$P=3.9$ atm.

$R=0.0821$

$$V=\frac{1.3 \text{ mole}\times 0.0821 \text{ litre atm. mole}^{-1}\times 312\text{K}}{3.9 \text{ atm.}}$$

$V=8.5$ litres.

Problem 2.2. Gas A diffuses through and opening at the rate of 30 c.c. per minute. Gas B diffuses through the same opening at the rate of 15 c.c. per minute. Which gas is heavier? The density of A is 1.0 g/l. Calculate the density of B, pressure and temperature are the same for both gases.

Solution. Let the rate of diffusion of gas A be r_A and that of B be r_B. According to Graham's law of diffusion

$$\frac{r_A}{r_B}=\sqrt{\frac{d_B}{d_A}}$$

$$\frac{30}{15}=\sqrt{\frac{d_B}{1.0 \text{ g}/l}}$$

$$\therefore \quad 4=\frac{d_B}{1.0 \text{ g}/l}$$

$d_B=4.0$ g/l.

Gas B is heavier and density d_B of B is 4.0 g/l.

Problem 2.3. A cylinder having a volume of 25.0 litres contains a gas at a pressure of 6.78×10^6 Pa and a temperature of 25°C. Assuming the gas to be ideal, how many moles of gas are there in the cylinder?

Solution. $PV=nRT$

$P=6.78\times 10^6$ Pa

$V=25.0\ l$

$T=298$ K

$$n=\frac{PV}{RT}=\frac{6.78\times 10^6\times 2.50\times 10^{-2}}{8.314\times 298}$$

$n=68.4.$

Problem 2.4. A gas balloon having a volume of 10.0 litre at 25°C and 1 atm. pressure rises to an altitude where the temperature is -10.0°C and the pressure is 500 mm Hg. What is the volume of the balloon at this altitude?

Solution.
$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$$

$P_1=1$ atm.$=760$ mm Hg

$T_1=228$ K

$$V_1=10.0\ l$$
$$P_2=500 \text{ mm Hg}$$
$$T_2=263 \text{ K}$$
$$V_2=?$$
$$V_2=\frac{P_1V_1\times T_2}{T_1P_2}$$
$$V_2=\frac{760\times 10.0\times 263}{298\times 400}$$
$$V_2=13.4 \text{ litre.}$$

Problem 2.5. Calculate the r.m.s. velocity of CO_2 molecules at 27°C (Mol. wt. of $CO_2=44$).

Solution. Root mean square velocity $\bar{C}=\sqrt{\dfrac{3RT}{M}}$

where $M=44$

$$R=8.31\times 10^7 \text{ ergs deg}^{-1}\text{ mole}^{-1}$$
$$T=273+27=300\text{K}$$
$$\bar{C}=\sqrt{\frac{3\times 8.31\times 10^7\times 300}{44}}$$
$$=4.15\times 10^4 \text{ cm s}^{-1}.$$

Problem 2.6. Calculate the temperature at which oxygen molecules will have the same r.m.s. velocity as carbon dioxide molecules at 27°C.

Solution. $\bar{C}_{CO_2}=\bar{C}_{O_2}$

$$M_{CO_2}=44$$
$$M_{O_2}=32$$
$$T_{O_2}=?$$
$$T_{CO_2}=300 \text{ K}$$
$$\bar{C}_{CO_2}=\sqrt{\frac{3RT_{CO_2}}{M_{CO_2}}}$$
$$=\sqrt{\frac{3R\times 300}{44}}$$
$$\bar{C}_{O_2}=\sqrt{\frac{3RT_{O_2}}{32}}$$

since $\bar{C}_{O_2}=\bar{C}_{CO_2}$

$$\sqrt{\frac{3RT_2}{32}}=\sqrt{\frac{3\times 300}{44}}$$
$$T_{O_2}=\frac{32\times 300}{44}=218.2 \text{ K}$$

Problem 2.7. What is the volume occupied by 3.50 g Cl_2 (g) at 45°C and 745 torr?

Solution. $P = 745 \text{ torr} \times \dfrac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$

$$V = ?$$

$$n = 3.5 \text{ g } Cl_2 \times \frac{1 \text{ mole } Cl_2}{70.9 \text{ g } Cl_2}$$

$$n = \frac{3.50}{70.9} \text{ mole } Cl_2$$

$$n = 0.0494 \text{ mole } Cl_2.$$

$$R = 0.0821 \text{ l atm mol}^{-1} \text{ K}^{-1}$$

$$T = 273 + 45 = 318 \text{ K}$$

Since $\quad PV = nRT$

$$V = \frac{nRT}{P}$$

$$\therefore \quad V = \frac{0.0494 \times 0.0821 \text{ l atm} \times 318 \text{ K}}{0.980 \text{ atm mol K}}$$

$$V = 1.32 \text{ l}$$

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Problem 2.8. A meteorological balloon had a radius of 1 m when released from sea level and expended to a radius of 3 m when it had risen to its maximum altitude where the temperature was —20°C. What is the pressure inside the balloon at that height?

Solution. We know that for an ideal gas $P_1V_1 = nRT_1$ *and* $P_2V_2 = nRT_2$

$$\frac{P_1V_1}{nRT_1} = 1 = \frac{P_2V_2}{nRT_2}$$

$$\therefore \quad P_2 = \left(\frac{V_1}{V_2}\right)\left(\frac{T_2}{T_1}\right)P_1$$

$$V_2 = \frac{4}{3}\pi R_2^3;$$ where R_2 is radius of the balloon at the maximum altitude.

$$V_1 = \frac{4}{3}\pi R_1^3,$$

$$\therefore \quad P_2 = \left(\frac{R_1}{R_2}\right)^3\left(\frac{T_2}{T_1}\right)P_1$$

$$R_1 = 1, R_2 = 3, P_1 = 1 \text{ atm}, T_2 = 253 \text{ K}$$

$$T_1 = 298 \text{ K}$$

$$\therefore \quad P_2=\left(\frac{1}{3}\right)^3\times\left(\frac{253\text{ K}}{298\text{ K}}\right)\times 1\text{ atm}$$

$$=0.031\text{ atm}$$

Problem. 2.9. A glass vessel weighs 40.1305 g when clean, dry, and evacuated; 138.2410 g when filled with water at 25°C ($d=0.9970$ g/cm^3) and 40.2487 g when filled with a gaseous substance at 740.4 torr and 24.1° C. What is the molecular weight of the gas?

Solution. Weight of water to fill the vessel

$$=138.2410\text{ g}-40.1305\text{ g}=98.1105\text{ g}$$

Volume of water (volume of vessel)

$$=98.1105\text{ g H}_2\text{O}\times\frac{1\text{cm}^3\text{ H}_2\text{O}}{0.9970\text{ g H}_2\text{O}}$$

$$=98.41\text{ cm}^3$$

$$=0.09841\text{ l}$$

Weight of the gas $=40.2487\text{ g}-40.1305\text{ g}$

$=0.1182\text{ g}$

Temperature $=273.15+24.1°\text{C}=297.2\text{ K}$

Pressure $=740.4\ \text{torr}\times\frac{1\text{ atm}}{760\text{ torr}}=09742\text{ atm}$

$$M=\frac{mRT}{P\ V}$$

$$M=\frac{0.1182\times 0.08206\text{l atm}\times 297.2\text{ K}}{0.9742\text{ atm mol K}\times 0.09841\text{ l}}$$

$$=30.07\text{ g/mole}$$

Problem. 2.10. What is the pressure of a mixture of 1 g of hydrogen and 1.4 g of nitrogen stored in 5dm^3 vessel at 127°C?

Solution. Pressure exerted by hydrogen, $p_{H_2}=\frac{0.5\times 8.31\times 400}{5\times 10^{-3}}$

$=3.33\times 10^5\text{ Nm}^{-2}$

Pressure exerted by nitrogen, $p_{N_2}=\frac{0.05\times 8.31\times 400}{5\times 10^{-3}}$

$=0.33\times 10^5\text{ Nm}^{-2}$

total pressure, $P=p_{H_2}+p_{N_2}=(3.33+0.33)\times 10^5\text{ Nm}^{-2}$

$=3.66\times 10^5\text{ Nm}^{-2}$

Problem 2.11. What weight of oxygen would be required to fill 2 dm^3 flask at 20°C and 9×10^4 Nm^{-2} pressure, if R has the value

$8.31\ \text{JK}^{-1}\ \text{mol}^{-1}$?

Solution. Since $PV = nRT$

$$n = \frac{PV}{RT} = \frac{9 \times 10^4 \times 2 \times 10^{-3}}{8.31 \times 293} = 0.074 \text{ mole}$$

Since 1 mole of oxygen weighs 32.0 g, the weight required is

$$0.74 \times 32 = 2.37 \text{ g}.$$

Problem 2.12. Compare the r.m.s. velocities of oxygen and carbon dioxide molecules at 27°C.

Solution. $T = 300$ K

$$\bar{C}_{CO_2} = \sqrt{\frac{3\,RT}{M}}$$

$$= \sqrt{\frac{3\,R \times 300}{44}}$$

$$= 30\sqrt{\frac{R}{44}}$$

$$\bar{C}_{O_2} = \sqrt{\frac{3\,RT}{M}}$$

$$= \sqrt{\frac{3 \times R \times 300}{32}}$$

$$= 30\sqrt{\frac{R}{32}}$$

$$\frac{\bar{C}_{CO_2}}{\bar{C}_{CO_2}} = \frac{30\sqrt{R}}{\sqrt{44}} \times \frac{\sqrt{32}}{30\sqrt{R}}$$

$$\frac{\bar{C}_{CO_2}}{\bar{C}_{O_2}} = 0.8527.$$

Problem 2.13. Determine the root mean square velocity of H_2 gas at 298 K.

Solution. $\bar{C} = \sqrt{\frac{3\,RT}{M}}$

$M = 2.0 \text{ g mol}^{-1} = 0.0020 \text{ kg mol}^{-1}$

$$R = 8.314 \text{ joules deg}^{-1} \text{ mol}^{-1}$$

$$\bar{C} = \sqrt{\frac{3(8.314)\,(298)}{(0.0020)}}$$

$$\bar{C} = 1930 \text{ m sec}^{-1}.$$

Problem 2.14. A certain volume of the gas evolved by a photosynthesis algal culture took 231*s* to stream through a small hole. Under precisely the same conditions, an equal volume of argon took 258*s*. Calculate (*a*) the molecular weight, and (*b*) the vapour density of the unknown gas (Molecular weight of argon=40).

Solution. According to Graham's law

$$\frac{t_1}{t_2}=\sqrt{\frac{M_1}{M_2}}$$

For the unknown gas	For argon
$t_1=231s$	$t_2=258s$
$M_1=?$	$M_2=40$

$$\frac{231}{258}=\sqrt{\frac{M_1}{40}}$$

$$M_1=\left(\frac{231}{258}\right)^{1/3}\times 40$$

Thus, (*a*) the molecular weight of the unknown gas=32.

(*b*) Vapour density of the unknown gas $= \frac{1}{2}$ molecular weight

$$= \tfrac{1}{2}\times 32$$

$$= 16.$$

Problem 2.15. Calculate the collision properties, σ, L, Z_1 and Z_{11} for nitrogen molecules at 1 atm. and 25°C. The viscosity of nitrogen $\eta = 178\times 10^{-6}$ poise.

Solution. The number of molecules in 1 c.c. at 25°C and 1 atm. is

$$n^{*}=\frac{6.024\times 10^{23}}{22{,}414\times(298.16/273.16)}$$

$$= 2.462\times 10^{19}$$

The average molecular speed is

$$\bar{C}_{av}=\sqrt{\frac{8\times 8.314\times 10^{7}\times 298.16\times 7}{22\times 28.02}}$$

$$= 0.475\times 10^{5}\text{ cm/sec.}$$

and the mass of one molecule is

$$m=\frac{28.02}{6.024\times 10^{23}}=4.65\times 10^{-23}\text{ g.}$$

$$\sigma=\sqrt{\frac{\bar{C}_{av}m}{2\sqrt{2}\pi\eta}}$$

$$=\sqrt{\frac{0.475\times 10^{5}\times 4.65\times 10^{-23}\times 7}{2\times\sqrt{2}\times 22\times 178\times 10^{-6}}}$$

$$\sigma = 3.74\text{Å}$$

$$L=\frac{1}{\sqrt{2}\pi\sigma^2 n^*}$$

$$L=\frac{7}{\sqrt{2}\times 22\times(3.74)^2\times 2.462\times 10^{19}}$$

$$L=6.50\times 10^{-6}\text{ cm}=650\text{ Å}.$$

$$Z_1=Z\sqrt{2}\pi\sigma^2\overline{C}_{av}n^*$$

$$=7.31\times 10^9\text{ collisions/sec.}$$

$$Z_{11}=\frac{1}{\sqrt{2}}\pi\sigma^2\overline{C}_{av}(n^*)^2$$

$$Z_{11}=8.99\times 10^{28}\text{ collisions/c.c. sec.}$$

Problem 2.16. Calculate the kinetic energy of oxygen molecules at 27°C and 127°C. What conclusions you draw from these values?

Solution. At 27°C K.E. $=\frac{3}{2}RT=\frac{3}{2}\times R\times 300$

$$=\tfrac{3}{2}\times 150\times 8.31\times 10^7$$

$$=450\times 8.31\times 10^7$$

$$=3.74\times 10^9\text{ ergs}=374\text{ joules.}$$

At 127°C K.E. $=\frac{3}{2}\times RT=\frac{3}{2}\times 8.31\times 10^7\times 400$

$$=4.986\times 10^9\text{ ergs}=498.6\text{ joules.}$$

Conclusion. Kinetic energy increases with the increase in temperature.

Problem 2.17. One mole of ammonia was found to occupy 2.5 litres at 27°C. Calculate the pressure that would have been exerted by it (*a*) using van der Waal's equation ($a=4.0$ litre atm mole^{-2}, $b=0.036$ litre mole^{-1}) and (*b*) using ideal gas equation.

Solution. (*a*) Using van der Waal's equation

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

$n=1$, $a=4.0$ litre atm mole^{-2}, $b=0.036$ litre mole^{-1}, $R=0.0821$ litre atm mole^{-1} deg^{-1}

$$\left(P+\frac{4}{6.25}\right)(2.5-0.036)=0.0821\times 300$$

$$=\left(P+\frac{16}{25}\right)(2.464)=300\times 82\times 10^{-4}$$

$$=\left(P+\frac{16}{25}\right)(2.464)=24.63\times 10^{-1}$$

$\therefore\quad P=9.936$ atm.

(*b*) Using ideal gas equation

$$PV = RT$$

$$R = 0.082 \text{ litre atm mole}^{-1} \text{ deg}^{-1}$$

$$P = \frac{0.082 \times 300}{2.5} = 9.84 \text{ atm.}$$

Problem 2.18. A gas obeys the van der Waal's equation, with $P_c = 30$ atm and $T_c = 200$°C. The compressibility factor PV/RT will be more than one (at $P=50$ atm, $T=250$°C; at $P=1$ atm, $T=100$°C; $P=500$ atm, $T=500$°C; none of these). The gas will approach ideality at (low temperature, low density, low values of the compressibility factor, none of these). Calculate the van der Waal's constant b for this gas.

Solution. $\frac{PV}{RT}$ should be greater than one at the highest P and T choice, 500 atm and 500°C as both, the first especially are far above the critical values. Ideality will be approached at low density. Since van der Waals gas $P_cV_c/RT_c = \frac{3}{8}$, and $b = V_c/3$, then

$$b = 0.082 \times \frac{473}{8} \times 30$$

$$= 0.163 \text{ litre/mole.}$$

Problem 2.19. Calculate the pressure exerted by one mole of acetylene at 27°C in a flask whose volume is 0.800 litre, using van der Waal's equation. The values for van der Waal's constant are 4.17 and 0.0371 respectively.

Solution. Since $n=1$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$\left(P + \frac{4.17}{(0.8)^2}\right)(0.8 - .0371) = 0.0820 \times 300$$

Units

$$\left(\text{atm} + \frac{\text{litre}^2\text{-atm} \times \text{mole}^2}{\text{litre}^2 \times \text{mole}^2}\right)\left(\text{litre-mole} \times \frac{\text{litre}}{\text{mole}}\right)$$

$$= \text{mole} \times \frac{\text{litre-atm}}{\text{K-mole}} \times \text{K}$$

$$\text{atm} \times \text{litre} = \text{litre} \times \text{atm}$$

$$\therefore 0.763\, P + \frac{4.17 \times 0.763}{0.640} = 24.6$$

$$P = \frac{24.6 - 4.98}{0.763} = 25.4 \text{ atm}$$

Problem 2.20. According to the estimate of molecular size given by van der Waal's equation, what is the fraction of the oxygen gas at 1 atm at 25°C actually occupied by oxygen molecules? The value of molecular diameter for oxygen is 2.93 Å.

Solution. Each oxygen molecule has a diameter of 2.93 Å. Each molecule has a volume of $\frac{4\pi r^3}{3} = \frac{4\pi}{3}\left(\frac{2.93}{2}\right)^3 = 13.2 \text{ Å} = 1.3\times10^{-23}$ cm³. Now let us consider 1 mol of the gas;

Volume at 1 atm and at 25°C $= 22{,}400 \text{ cm}^3 \times \frac{298}{273} = 24{,}400 \text{ cm}^3$

Numbers of molecules $= N = 6.02\times10^{23}$

Volume of N molecules $= 6.02\times10^{23}\times1.32\times10^{-23} \text{ cm}^3 = 7.9 \text{ cm}^3$

The per cent of total volume occupied by O_2 molecule is

$$\frac{7.9}{24{,}400}\times100 = 0.032 \text{ per cent.}$$

Problem 2.21. One mole of carbon dioxide is found to occupy $0.382\times10^{-3}\text{m}^3$ at 40°C and under a pressure of $5.4\times10^6 \text{ Nm}^{-2}$. Calculate the pressure that the gas would exert using (*i*) the ideal gas equation, (*ii*) the van der Waal's equation. The values of a and b are 0.36 and 4.28×10^{-5} respectively.

Solution. (*i*) Since $PV = nRT$

$$P = \frac{8.31\times313}{0.382\times10^{-3}}\times6.8\times10^6 \text{ Nm}^{-2}$$

(*ii*)

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$P = \frac{8.31\times313}{(0.382\times10^{-3}-4.28\times10^{-5})} - \frac{0.36}{(0.382\times10^{-3})^2}$$

$$P = 5.18\times10^6 N\text{m}^{-2}$$

EXERCISES

2.1. Select the best term associated with each definition, description, or specific example. Terms (A) Brownian motion; (B) effusion; (C) inelastic collision; (D) solution; (E) van der Waals forces.

(*a*) characterised by a net loss of momentum

(*b*) escape of air through a pin hole from an air tank in outer space

(*c*) attractions between neighbouring molecules in a substance

(*d*) a homogeneous mixture

(*e*) jostling of microscopic particles dispersed in a fluid caused by collisions with atoms, molecules or ions.

[**Ans** *a*. (C), *b*. (B), *c*. (E), *d*. (D) and *e*. (A).]

2.2. Select the term best associated with each definition, description or specific example. Terms (A) critical temperature; (B) boiling point; (C) miscible; (D) vapour pressure; (E) viscometer.

(*a*) for water at 100°C, this is 760 torr.
(*b*) for water at 760 torr, this is 100°C.
(*c*) above this point no pressure is great enough to produce a two-phase system.
(*d*) instrument used to measure resistance to flow for a fluid.

[**Ans.** *a*. (D) *b*. (B), *c*. (A) and *d*. (E).]

2.3. A gas occupies a volume of 250 c.c. at a pressure of 742 mm Hg. What volume will it occupy, at the same temperature at a pressure of 10 mm Hg.

[**Ans.** 1.86×10^4 c.c.]

2.4. Match the laws in the first column with the mathematical expressions in the second.

(*a*) Boyle's law	(*i*) $\frac{V_1}{V_2} = \left(\frac{m_2}{m_1}\right)^{\frac{1}{2}}$
(*b*) Charle's law	(*ii*) $V = cT$
(*c*) Ideal gas law	(*iii*) $P_1 = X_1 P$
(*d*) van der Waal's equation	(*iv*) $\left(P + \frac{a}{V^2}\right)(V - b) = RT$
(*e*) Law of partial pressure	(*v*) $PV = nRT$
(*f*) Graham's law	(*vi*) $PV = a$

[**Ans.** (*a*) (*vi*), (*b*) (*ii*), (*c*) (*v*), (*d*) (*iv*), (*e*) (*iii*), (*f*) (*i*)]

2.5. Which expressions on the right correspond with the terms on the left?

(*a*) root mean square velocity	(*i*) $3/2\ RT$
(*b*) average velocity	(*ii*) $\left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$
(*c*) heat capacity for a monoatomic gas	(*iii*) $(3kT/m)^{\frac{1}{2}}$
(*d*) kinetic energy for a monoatomic gas	(*iv*) $\frac{3}{2}R$
(*e*) mole fraction	(*v*) $n_i/\Sigma n$

[**Ans.** (*a*) (*iii*), (*b*) (*ii*), (*c*) (*iv*), (*d*) (*i*), (*e*) (*v*).]

2.6. Two grams of O_2 are in a 2 litre vessel by a pressure of 1.21 atm. What is the temperature of the gas in °C?

[**Ans.** 200°C.]

2.7. At 0°C and under a pressure of 1000 mm Hg, a given weight of N_2 occupies a volume of 1 litre. At −100°C the same weight of gas under the same pressure occupies a volume of 0.6313 litre. Calculate the absolute zero in degrees centigrade and give reasons for the observed difference from the accepted value.

[**Ans.** −271.2°C.]

2.8. The time required for a given volume of N_2 to diffuse through an orfice is 35 sec. Calculate the molecular weight of the gas which requires 50 seconds to diffuse through the same orifice under identical conditions.

[**Ans.** 57.15 g/mole.]

2.9. A flask having a volume of 250 ml and containing air is heated to 100°C and then sealed. The flask is cooled to 25°C, immersed in water, and opened. What volume of water will be drawn back into the flask, assuming the pressure remains constant? [**Ans.** 50 ml.]

2.10. Calculate the pressure exerted by 35 g of carbon dioxide in a one litre vessel at 24°C, using the ideal gas law. [**Ans.** 19.4 atm.]

2.11. 500 c.c. of N_2 at 700 mm of Hg pressure and 100 c.c. of CO_2 at 600 mm Hg pressure are placed in two-litre flask at 25°C. Calculate the final gas pressure in the flask. [**Ans.** 0.625 atm.]

2.12. One gram of N_2 and one gram of O_2 are contained in a two-litre flask at 27°C. Calculate the partial pressure exerted by each gas and the total pressure in the flask.

[**Ans.** $p_{N_2}=0.44$ atm, $p_{O_2}=0.385$, $P_{\text{total}}=0.825$ atm.]

2.13. Calculate the volume occupied by a mixture of 14 g nitrogen and 16 g. oxygen at 8.3×10^5 Nm^{-2} at 127°C. [**Ans.** 4dm^3]

2.14. Calculate the root mean square velocity of the molecules in methane at 127°C and 1.013×10^5 Nm^{-2} pressure. [**Ans.** 79000 cms^{-1}.]

2.15. How many moles of nitrogen must be added to a mixture of 4 g. of hydrogen and 14 g of carbon monoxide contained in a 50 dm^3 flask at 27°C to bring the total pressure up to 1.5 atm? [**Ans.** 0.55 mole]

2.16. A two-litre flask containing carbon dioxide at 60 cm pressure is connected to a four-litre flask containing nitrogen at 48 cm pressure. If the temperature is kept constant, calculate the final pressure of the mixture.

[**Ans.** 52 cm]

2.17. What is the mole fraction of nitrogen in a mixture of nitrogen and hydrogen in which the final pressure of hydrogen is 63 cm and the total pressure is 90 cm? [**Ans.** 0.3.]

2.18. Assuming that air behaves as an ideal gas, calculate exactly the weight of 1 ml of air at 25° and 1 atm if the relative humidity of the air is 70 per cent and the vapour pressure of water at 25° is 23.7 mm. The composition of dry air is 80 per cent nitrogen and 20 per cent oxygen by volume. The buoyancy of air is about 0.0012 gram per ml at a room temperature.

[**Ans.** 11.69×10^{-4} g ml^{-1}.]

2.19. Calculate the temperature at which the root mean square velocity of a nitrogen molecule is the same as that of a helium molecule at 27°C.

[**Ans.** 2100 K.]

2.20. A cylinder contains nitrogen gas and a small amount of liquid water at a temperature of 25°C (the vapour pressure of water at 25°C is 23.8 mm). The total pressure is 600 mm Hg. A piston is pushed into the cylinder until the volume is halved. What is the final total pressure?

[**Ans.** 1176 mm.]

2.21. Calculate the kinetic energy for 10 moles of an ideal gas at 27°C.

[**Ans.** 9.0 k. cal.]

2.22. Calculate the root mean square velocity of oxygen molecules at 15°C and 770 mm pressure. [**Ans.** 4.74×10^4 cm sec^{-1}.]

2.23. The molecular diameter of carbon monoxide is 3.19×10^{-8} cm. At 27°C and a pressure of 250 mm what will be (*i*) the number of molecules colloiding per cubic centimetre per second; (*ii*) the number of bimolecular collisions; and (*iii*) the mean free path.

(**Ans.** (*i*) 2.54×10^{29}; (*ii*) 1.27×10^{29}; (*iii*) 2.75×10^{-5} cm.]

2.24. Calculate the average kinetic energy of translation of a molecule of a gas at 27°C (*i*) in calories and (*ii*) in ergs.

[**Ans.** (*i*) 1 5 $\times 10^{-21}$ cal; (*ii*) 6.27 $\times 10^{-11}$ erg.]

2.25. Calculate the translational kinetic energy of O_2 at (*i*) 300 k (*ii*) 1000 K.

[**Ans.** (*i*) 3740 J mole^{-1}; (*ii*) 12.5 k J mole^{-1}.]

2.26. Two flasks of equal volume are connected by a narrow tube of negligible volume. Initially both the flasks are at 27°C and contain 0.70 mole of hydrogen gas, the pressure being 0.50 atm. One of the flasks is then immersed in a hot oil bath at 127°C, while the other is kept at 27°C. Calculate the final pressure of and the moles of hydrogen in each flask.

[**Ans.** 0.57 atm, 0.4 mole, 0.3 mole.]

2.27. A real gas of molecular weight 150, obeys the van der Waals equation its critical pressure and temperature are 100 atm and 100°C, respectively. Calculate the value of the compressibility factor at the critical point.

[**Ans.** 3/8.]

2.28. Calculate the root mean square velocity of mercury atoms whose kinetic energy is 1.00 k. cal mole^{-1}. [**Ans.** 2.04 $\times 10^{2}$ ms^{-1}.]

2.29. It is found experimentally that 10.0 moles of O_2 at 100 atm pressure and 273 K occupies a volume of 2.08 l. Calculate the compressibility factor for O_2 at this temperature and pressure. [**Ans.** 0.928]

2.30. Determine the pressure in atmospheres exerted by 1 mole of steam confined to a 1.0 litre container at 150°C using van der Waals equation. Show that this pressure is less than that of an ideal gas under similar conditions. The van der Waals constants *a* and *b* for steam are 5.46 l^{-2} atm mole^{-2} and 0.0305 l mole^{-1}. [**Ans.** 30.4 atm, 34 7 atm.]

2.31. The time required for a given volume of N_2 to diffuse through an orifice is 35 seconds. Calculate the molecular weight of a gas which requires 50 seconds to diffuse through the same orifice under identical conditions.

[**Ans.** 57.15 g/mole.]

2.32. Calculate, according to van der Waals equation, the pressure that would have to be applied to N_2 to reduce the total volume to a value equal to four times the excluded volume (*a*) at a temperature of 25°C; (*b*) at a temperature of 1000°C. [**Ans.** (*a*) 151 atm, (*b*) 835 atm.]

2.33. Calculate, L, σ, Z_1 and Z_{11} for water vapour at 150°C and 1 atm pressure. The coefficient of viscosity of water vapour is 144.5 poise.

[**Ans.** 7.88 $\times 10^{-8}$ m, 1.733 $\times 10^{25}$ m^{-3}, 8.95 $\times 10^{9}$ s^{-1}, 7.75 $\times 10^{34}$ s^{-1} m^{-3}.]

2.34. If the radius of an argon atom is 1.54 $\times 10^{-8}$ cm, what per cent of the total volume occupied by one mole of argon gas at STP is empty space?

[**Ans.** 99.96%.]

2.35. Using the Beattie-Bridgeman equation explicit in volume, calculate the density in grams per cubic centimetre of N_2 at 0°C and 100 atm pressure.

[**Ans.** 0.127 g/c.c.]

2.36. Employing the Kamerlingh Onnes equation of state find the compressibility factor of carbon monoxide at −50°C and 10 atm pressure. [**Ans.** 0.981.]

2.37. A gas whose viscosity is 200 micropoises flows through a capillary tube 2 mm in diameter and 2 metres long. If 5 litres of gas pass through the tube every 10 seconds, what must be the pressure head under which the gas is flowing? [**Ans.** 5.09 $\times 10^{5}$ dynes/cm^{2}.]

2.38. For oxygen at 25°C calculate the number Z of collisions per second per molecule, the number Z of collisions per cubic metre per second and the number of moles of collisions per litre per second at a pressure of 1 atm. The molecular diameter of oxygen is 3.61Å.

[**Ans.** $Z=6.32\times10^{9}\ s^{-1}$, $Z=7.77\times10^{34}$ collisions $m^{-3}\ s^{-1}$ and 1.29×10^{8} mol $litre^{-1}\ s^{-1}$.]

2.39. For oxygen at 25° calculate the mean free path at (*a*) 1 atm pressure and (*b*) 10^{-3} torr. Given n is equal to 2.46×10^{25} molecules m^{-3}.

[**Ans.** (*a*) 7.02×10^{-8} m, and (*b*) 5.3 cm.]

2.40. Large vacuum chambers have been built for testing space vehicles at 10^{-8} torr. Calculate (*a*) the mean free path of nitrogen at this pressure and (*b*) the number of molecular impacts per m^2 of wall per second at 25°. $\sigma n=$ 3.75Å.

[**Ans.** (*a*) 4.94×10^{3} m, and (*b*) $3.84\times10^{16}\ m^{-2}\ s^{-1}$.]

2.41. The molecular diameter of CO is 3.19×10^{-9} cm. At 27°C and a pressure of 250 mm what will be (*a*) the number of molecules colliding per cubic, centimetre per second, (*b*) the mean free path?

[**Ans.** (*a*) 2.54×10^{29} molecules colliding per cm^3 per sec, and (*b*) 2.75×10^{-5} cm.]

2.42. The critical temperature of CCl_4 is 283.1°. The densities in gram per cm^3 of the liquid ρ_l and vapour ρ_v at different temperatures are as follows:

t	100°	150°	200°	250°	270°	280°
ρ_l	1.4343	1.3215	1.1888	0.9980	0.8666	0.7634
ρ_v	0.0103	0.0304	0.0742	0.1754	0.2710	0.3597

Calculate the critical molar volume of CCl_4? [**Ans.** 276 cm^3 $mole^{-1}$.]

2.43. Show that to a first approximation the equation of state of a gas which demerises to a small extent is given by

$$\frac{P\tilde{V}}{RT}=1-\frac{K_c}{\tilde{V}}$$

where K_c is the equilibrium constant for the formation of dimer.

$$2A=A_2$$

$$K_c=\frac{[A_2]}{[A]^2}$$

2.44. Using van der Waals equation, calculate the volume occupied by (*a*) 1 mole of ethylene, (*b*) 1 g of ethylene at 10 atm and 0°C. Given for ethylene $a=4.47$ atm $litre^2$ $mole^{-2}$ and $b=0{,}0571$ litre $mole^{-1}$.

[**Ans.** (*a*) 2.084 litre, (*b*) 0.0744 litre.]

2.45 The critical constants $T_c.P_c$ and V_c for water are 374°C, 218 atm and 0.0566 litre $mole^{-1}$ respectively. Calculate the values of a, b, and R.

[**Ans.** $a=2.1$ atm $mole^{-1}$ K^{-1}; $b=1.89\times10^{-2}$ litre $mole^{-1}$; and $R=5.09\times10^{-2}$ litre atm $mole^{-1}$ K^{-1}.]

The van der Waals constant b for helium is 24 cm^3/mole. Calculate the molecular diameter of helium. [**Ans.** 2.67×10^{-10} m.]

2.46. The critical temperature T_c and critical pressure P_c for argon are −122.44°C and 48 00 atm respectively. Calculate the van der Waals constants a and b.

[**Ans.** $a=1.358$ $litre^2$ atm $mole^{-2}$; and $b=3.24\times10^{-2}$ litre $mole^{-1}$.]

3

CHEMICAL THERMODYNAMICS—I

INTRODUCTION

Thermodynamics deals with the study of mechanical action produced by heat. It is concerned with the relationship between the energy changes that occurs in chemical and physical processes. Several chemical reactions are carried out for the sole purpose of producing energy, *i.e.*, combustion of fuels such as gasoline and coal and the generation of electricity by means of battery. In addition to practical applications, there are important theoretical relationships between energy and chemical change.

Work. It is a means of transferring energy that results in a displacement against opposition. Displacement × opposition = distance × force. Of interest to chemists is pressure--volume work.

Heat. It is a means of transferring energy other than by work. Transfer of heat from a source to a receiver requires a temperature difference between the two, and the quantity of heat transferred is calculated from the temperature change multiplied by the heat capacity.

Internal energy. The internal energy of a system is the sum of the various kinetic and potential energy contributions. The determination of absolute value of internal energy is difficult and most of the calculations and experimental determination are concerned with the change in the internal energy, *i.e.*

$$\triangle E = E_{final} - E_{initial} \qquad \ldots (1)$$

It is a function of state.

Enthalpy. It is defined as

$$H = E + PV \qquad \ldots (2)$$

change in enthalpy $\triangle H$ is given by,

$$\triangle H = \triangle E + P\triangle V \qquad \ldots (3)$$

Since, $P\triangle V = W$, and $\triangle H = q_p$. Relation (3) can therefore be written as

$$q_p = \triangle E + P\triangle V \qquad \ldots (4)$$

$$\triangle E = q_v$$

$$q_p = q_v + P\triangle V \qquad \ldots (5)$$

First Law of Thermodynamics

First law of thermodynamics which is also known as the law of conservation of energy states that energy can neither be created nor destroyed, but may be converted from one form to another. Mathematically,

$$\triangle E=q+w \qquad \ldots (6)$$

Work done in an isothermal expansion. The amount of work done in an isothermal reversible expansion of a gas from volume V_1 to V_2 is given by

$$W=RT\ ln\ V_2/V_1 \qquad \ldots (7)$$

Work done in an adiabatic expansion. The work done in an adiabatic reversible expansion is given by

$$P_1V_1^{\gamma}=P_2V_2^{\gamma} \qquad \ldots (8)$$

where $\gamma=C_p/C_v$

C_p is the heat capacity of a gas at constant pressure and C_v is the heat capacity at constant volume.

Thermochemistry

It deals with the measurement of heat changes accompanying chemical reactions. A reaction, before it can be subjected to thermochemical measurements, must satisfy the following criteria:

(*i*) the reaction must be complete,
(*ii*) the reaction must be fast,
(*iii*) the reaction must be clean.

Only a few reactions fulfil all these conditions. Consider a reaction

$$\text{Reactants}\rightarrow\text{Products} \qquad \ldots (9)$$

Heat of reaction $\triangle H$ is the difference in the enthalpies of the reaction products and the reactants at constant pressure and at a definite temperature *i.e.*

$$\triangle H=H_{products}-H_{reactants} \qquad \ldots (10)$$

Reactions which occur with the evolution of heat ($\triangle H=$ —ve) are said to be exothermic and the reactions in which heat is absorbed ($\triangle H=$ +ve) are known as endothermic.

Laws of Thermochemistry. The calculation of heats of reaction and heats of formation have all been based on the first law of thermodynamics. There are two laws of thermochemistry.

According to the observations of A.L. Lavoisier and P.S. Laplace, the quantity of heat which must be supplied to decompose a compound into its elements is equal to the heat evolved when that compound is formed from its elements. In other words, the heat of decomposition of a compound is numerically equal to its heat of formation but of opposite sign *i.e.*

$$S(c)+O_2(g)=SO_2(g) \qquad \Delta H^\circ_{298}=-70.96 \text{ k. cal}$$

$$SO_2(g)=S(c)+O_2(g) \qquad \Delta H^\circ_{298}=70.96 \text{ k. cal}$$

As a consequence of this law, the thermochemical equations can be reversed by changing the sign of the heat term. However, its numerical value remains unchanged.

Hess's Law of Constant Heat Summation

This law states that the resultant heat change in a chemical reaction, carried out either at constant pressure or at constant volume is independent of the steps involved.

It follows from this law that if a reaction proceeds in more than one step then the enthalpy change in each step can be added and the sum is constant

$$CH_4(g)+Cl_2(g)=CH_3Cl(g)+HCl(g) \qquad \Delta H_1$$

$$CH_3Cl(g)+Cl_2(g)=CH_2Cl_2(g)+HCl(g) \qquad \Delta H_2$$

$$CH_2Cl_2(g)+Cl_2(g)=CHCl_3(g)+HCl(g) \qquad \Delta H_3$$

$$CHCl_3(g)+Cl_2(g)=CCl_4(g)+HCl(g) \qquad \Delta H_4$$

$$CH_4(g)+4Cl_2(g)=CCl_4(g)+4HCl(g) \qquad \Delta H_T$$

$$\therefore \quad \Delta H_T = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

A consequence of Hess's law is, that chemical equations can be added and subtracted like the algebraic equations. It is customary, to take standard state as 1 atmospheric pressure and 25°C. The enthalpy of elements in the standard state is arbitrarily taken as zero.

Relation between ΔE and ΔH of Reaction

$$\Delta H=\Delta E+\Delta n_g RT \qquad \ldots(11)$$

$$\Delta n_g=n_{products}-n_{reactants} \qquad \ldots(12)$$

Heat of formation. The heat of formation of a compound is defined as the increase of ethalpy when 1 mole of the compound is formed from its elements. It is denoted by ΔH°_f.

Heat of combustion. It is defined as the enthalpy change accompanying the complete combustion of 1 mole of a compound. Organic compounds containing carbon, hydrogen and oxygen can be burnt in oxygen to form carbon dioxide and water. The heats of combustion of both liquid and gaseous hydrocarbons are important from the industrial standpoint, and the term calorific value is frequently used for the heat of combustion of a substance as a fuel.

Heat of solution. The heat of reaction for dissolving one mole of solute in *n* moles of solvent is known as the heat of solution or integral heat of solution.

Heat of dilution. The heat of reaction for diluting one mole of solute in a solution of given concentration, by adding solvent to produce a solution of definite concentration, is known as the integral heat of dilution.

Effect of temperature on heat of reaction. The heat change associated with any process, physical or chemical, usually varies with temperature; the relationship of this variation is given by Kirchhoff's equation

$$\triangle H_2 = \triangle H_1 + \triangle C_p(T_2 - T_1) \qquad \ldots (13)$$

where $\triangle H_2$ and $\triangle H_1$ are the heats of reaction at constant pressure at the temperatures T_1 and T_2 respectively. $\triangle C_p$ is the mean molar heat capacity.

Bond energy. The bond energy is defined as the average amount of energy required to break a particular bond in a molecule producing free atoms or radicals. The mean bond energy in k. cal per mole for some bonds is given in Table 3.1.

TABLE 3.1. Representative bond energies

Bond	*Energy (k. cal)*
H—H	103
Cl—Cl	57
O=O	116
N≡N	225
O—H	109
N—H	92
C—H	98
H—Cl	102
Br—Br	45
I—I	36
H—I	71
C—Cl	78
H—Br	87
C—C	85

Problem 3.1. Calculate the work done when 2 moles of H_2 expands (*i*) isothermally against a constant pressure of 1 atm at 25°C from 15 litres to 50 litres (*ii*) the gas expands isothermally and reversibly.

Solution. $W = 2.303\ n\ RT \log V_2/V_1$

$$W = 2.303 \times 2 \times 1.98 \times 298 \log \frac{50 \times 2}{15 \times 2}$$

$$W = 4.606 \times 298 \times 1.98 \log \frac{100}{30}$$

$$W = 1830 \text{ calories.}$$

Work done in an isothermal process

$$W = P\triangle V$$
$$= P(V_2 - V_1)$$
$$= 1 \times (50 - 15)$$
$$= 35 \text{ Joules.}$$

(*i*) 1830 calories, (*ii*) 35 joules.

Problem 3.2. Calculate the maximum work done in ergs when one mole of an ideal gas expands from 10 litres to 20 litres at 25°C.

Solution. Work done in an isothermal reversible expansion of an ideal gas is given by

$$W = 2.303\, nRT \log V_2/V_1$$
$$n = 1 \text{ mole, } T = 273 + 25 = 298 \text{ K}$$
$$V_1 = 10 \text{ litres, } V_2 = 20 \text{ litres}$$
$$R = 1.98 \text{ cal. deg}^{-1} \text{ mol}^{-1}$$
$$W = 2.303 \times 1 \times 298 \times 1.98 \log \frac{20}{10}$$
$$W = 409.1 \text{ calories.}$$

Also,

$$W = JH$$
$$= 4.2 \times 10^7 \times 409.1$$
$$= 1.72 \times 10^{10} \text{ ergs.}$$

Problem 3.3. Two moles of an ideal gas initially at 27°C and one atm are compressed reversibly to half the initial volume. Calculate q, W, $\triangle E$ and $\triangle H$ when the process is carried on isothermally.

Solution. $W = 2.303\, nRT \log V_2/V_1$

$$T = 300 \text{ K}, \quad n = 1, \quad R = 1.98 \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$V_2 = \tfrac{1}{2} V_1$$
$$W = 2 \times 2.303 \times 1.98 \times 300 \log \tfrac{1}{2}$$
$$= 2 \times 2.303 \times 1.98 \times 300 \log \tfrac{1}{2}$$
$$W = -1914.0 \text{ cal.}$$

Since the process is being carried on isothermally *i.e.* no change of temperature,

$$\therefore \quad \triangle H = 0 \quad \text{and} \quad \triangle E = 0$$

According to 1st law of thermodynamics,

$$q = \triangle E + P\triangle V$$
$$q = \triangle E + W$$
$$q = 0 + W; \quad q = -1914 \text{ cal.}$$
$$W = -1914 \text{ cal}, \quad \triangle E = 0, \quad \triangle H = 0, \quad q = -1914 \text{ cal.}$$

Problem 3.4. Compute the work done in a diesel engine cylinder on the compression stroke if the frictionless path is assumed to be $PV^{1\cdot4}$=constant, and the volume decreases from 1 m³ to 0.05 m³. The initial pressure of air is 101.33 k *Pa*.

Solution. Since $PV^{1\cdot4}$=constant

$$P_1V_1^{1\cdot4}=P_2V_2^{1\cdot4}$$

and the pressure after compression will be

$$P_2=P_1\left(\frac{V_1}{V_2}\right)^{1\cdot4}$$

$$=101.33\left(\frac{1}{0.05}\right)^{1\cdot4}$$

$$=6717 \text{ k } Pa$$

The work done can be obtained by integrating the area under the $PV^{1\cdot4}$=constant path

$$W=\int_1^2 PdV=C\int_{V_1}^{V_2} V^{1\cdot4}dV$$

$$=C\left(\frac{V^{-1\cdot4}}{-0.4}\right)_1^2$$

Let $C=P_2V_2^{1\cdot4}$ as upper limit and at lower limit $C=P_1V_1^{1\cdot4}$.

$$W=\frac{P_2V_2^{1\cdot4}V_2^{-0\cdot4}-P_1V_1^{1\cdot4}V_1^{-0\cdot4}}{-0.4}$$

$$=\frac{P_2V_2-P_1V_1}{-0.4}$$

$$=\frac{(6717 \text{ k } Pa\times0.05 \text{ m}^3-101.33\times1)}{-0.04}$$

$$\times1 \text{ k } N/\text{m}^2 \text{ k } Pa\times1 \text{ k } J/\text{k } N\text{m}$$

$$=-586.3 \text{ k } J$$

The negative sign indicates that work is done on the system in order to accomplish compression.

Problem 3.5. Calculate (*a*) Q, (*b*) W, and (*c*) $\triangle E$ for the reversible adiabatic expansion of 1 mole of an ideal gas ($C_v=\frac{3}{2}R$) from 5.00 to 25.00 litres. The initial temperature is 27° C.

Solution. (*a*) $Q=0$ adiabatic

(*b*) and (*c*) $\triangle E=W=C_v(T_2-T_1)$ (adiabatic)

$$T_1(V_1)^{R/C_v}=T_2(V_2)^{R/C_v}$$

$$T_2 = T_1 (V_1/V_2)^{R/C_v}$$

$$= 300.0 \text{ K } (5/25)^{\frac{2R}{3R}}$$

$$= 300.0 \text{ K } (5/25)^{\frac{2}{3}}$$

$$T_2 = 102.6 \text{ K}$$

$$\triangle E = W = \tfrac{3}{2} R(T_2 — T_1)$$

$$= 1.500 \times 1.98 \ (102.6 — 300)$$

$$\triangle E = —588.4 \text{ cal/mol.}$$

Problem 3.6. Calculate the work done and the final volume in the following irreversible adiabatic expansion. Three moles of an ideal monoatomic gas expand irreversibly from an initial pressure of 5 atm against a constant external pressure of one atm until the temperature drops from the initial value of 350 K to final value of 275 K. How much work is done and what is final volume?

Solution. For monoatomic gas $C_v = 3$ cal deg^{-1} mole^{-1}

$$\triangle E = nC_v \ (T_2 — T_1)$$

$$= 3 \times 3 \ (275 — 350)$$

$$= —675 \text{ cal.}$$

The loss in internal energy must equal the work done in adiabatic expansion. To convert the calories to energy units in litre atm —575 calories= —27.8 litre-atm. Since work is done against a constant pressure,

$$W = —P(V_2 — V_1) = —(1)(V_2 — V_1) = 27.8 \text{ litre atm.}$$

$$V_1 = \frac{nRT}{P} = \frac{3 \times 0.082 \times 350}{5} = 17.2 \text{ litres.}$$

$$V_2 = 27.8 + 17.2 = 45.0 \text{ litres.}$$

Problem 3.7. Calculate the work done in the reversible compression of 10.0 g of He gas from an initial pressure of 1.00 atm to a final pressure of 5.00 atm at a constant temperature of 27°C.

Solution. The work done in an isothermal reversible expansion of a gas;

$$W = nRT \times 2.303 \log P_2/P_1$$

$$= \frac{10.0}{4} \times 1.987 \times 300 \times 2.303 \log 5$$

$$W = 2400 \text{ cal.}$$

Problem 3.8. Calculate the heat of combustion of one mole of benzene at constant volume, given that the heat of combustion at constant pressure is —781.0 k. cal at 25°C.

Solution. The combustion reaction is as follows:

$$C_6H_6(l)+\tfrac{15}{2}O_2(g)\rightarrow 6CO_2(g)+3H_2O(l)$$

$$q_p = -781.0 \text{ k. cal.}$$

$$\triangle n = 6 - 15/2 = -3/2$$

$$q_p = q_v + \triangle nRT$$

$$q_v = q_p - \triangle nRT$$

$$= -781.0 - (-\tfrac{3}{2})\,(1.98\times10^{-3}\times298)$$

$$= -781.0 + 0.8851$$

$$q_v = -780.1149 \text{ k. cal.}$$

$$q_v = -780.1149 \text{ k. cal.}$$

Problem 3.9. A 5 dm^3 bomb calorimeter was to be filled with sufficient oxygen under pressure to support the complete combustion of 36 g of glucose. When filled with oxygen at room temperature from the only available cylinder, the final pressure was only 7.1×10^5 Nm^{-2}. Would this be sufficient to allow complete combustion of sugar? (Room temperature was 290 K, *i.e.* 17°C, glucose $C_6H_{12}O_6$).

Solution. $P = 7.1\times10^5 \text{ Nm}^{-2}$

$V = 5 \text{ dm}^3 = 5\times10^{-3} \text{ cm}^3$

$R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$

$T = 290 \text{ K}$

$n = ? \text{ mole}$

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{(7.1\times10^5)\times(5\times10^{-3})}{8.314\times290}\text{mole}$$

$$= 1.47 \text{ mole.}$$

The complete combustion of glucose yields CO_2 and water

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$$

Six moles of O_2 would be required for the complete combustion of 1 mole of glucose. Thus for 0.2 mol of glucose 1.2 mol of oxygen would be required, and 5 dm^3 of O_2 at 7.1×10^5 Nm^{-2} being equal to 1.47 mol of O_2, would be sufficient.

Problem 3.10. The bacterium *Acetobacter suboxydans* may obtain energy for growth by oxidising ethanol first to acetaldehyde and then to acetic acid, according to following chemical reactions,

(*a*) $C_2H_5OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O$

(*b*) $CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH$

Calculate the values of $\triangle H$ (at 298 K) and standard atmospheric pressure for (*a*) and (*b*). Given the following heats of combustion at 298 K and standard atmospheric pressure, $C_2H_5OH = -1371$ kJ mole^{-1}, $CH_3CHO = -1168$ kJ mole^{-1} and $CH_3COOH = -876$ kJ mole^{-1}.

Solution. (*a*) The heats of combustion of ethanol and acetaldehyde help us to write the following reactions,

$$C_2H_5OH+3O_2\rightarrow 2CO_2+3H_2O \quad \Delta H=-1371 \text{ kJ mole}^{-1} \quad \ldots (i)$$

$$CH_3CHO+2\tfrac{1}{2}O_2\rightarrow 2CO_2+2H_2O \quad \Delta H=-1168 \text{ kJ mole}^{-1} \quad \ldots (ii)$$

On subtracting (*ii*) from (*i*)

$$C_2H_5OH+\tfrac{1}{2}O_2\rightarrow CH_3CHO+H_2O$$

$$\Delta H=(-1371)-(-1168) \text{ kJ mole}^{-1}$$

$$=-203 \text{ kJ mole}^{-1}.$$

(*b*) The combustion reactions of acetaldehyde and acetic acid proceed according to the following chemical reactions:

$$CH_3CHO+2\tfrac{1}{2}O_2\rightarrow 2CO_2+2H_2O \quad \Delta H=-1168 \text{ kJ mole}^{-1} \quad \ldots (iii)$$

$$CH_3COOH+2O_2\rightarrow 2CO_2+2H_2O \quad \Delta H=-876 \text{ kJ mole}^{-1} \quad \ldots (iv)$$

Subtracting (*iv*) from (*iii*) we get

$$CH_3CHO+\tfrac{1}{2}O_2\rightarrow CH_3COOH$$

$$\Delta H=(-1168)-(-876) \text{ kJ mole}^{-1}$$

$$=-292 \text{ kJ mole}^{-1}.$$

Hence ΔH for the oxidation of ethanol to acetaldehyde is —273 kJ mole^{-1} and acetaldehyde to acetic acid is —292 kJ mole^{-1}.

Problem 3.11. The standard heat of combustion of liquid ethanol is —326.7 k. cal at 25°C. Calculate its heat of formation from the elements in their standard state. Given that the heat of formation for CO_2 is —94.05 k. cal and for H_2O is —68.32 k. cal.

Solution. The combustion reaction for liquid ethanol can be written as

$$C_2H_5OH(l)+3O_2(g)=2CO_2(g)+3H_2O(l)$$

$$\Delta H=-326.7 \text{ k. cal.}$$

$$\Delta H=H_{products}-H_{reactants}$$

$$-326.7=\{2\times(-94.05)+3(-68.32)\}-\{(x+0)\}$$

$$-326.7=\{-188.1-204.96-x\}$$

$$x=-393.06+326.7=-66.36.$$

Thus the heat of formation of ethanol is —66.36 k. cal/mole.

Problem 3.12. Calculate the heat of formation of naphthalene when the standard heat of combustion of naphthalene is —1231.6 k. cal/mole at +25°C. Given that heats of formation of CO_2 and H_2O are 94.05 k. cal/mole and —68.32 k. cal/mole, respectively.

Solution. Combustion of naphthalene proceeds according to the following reaction,

$$\begin{array}{cccc} C_{10}H_8(s)+ & 12O_2(g)\rightarrow & 10CO_2(g)+4H_2O(l) \\ x & 0 & 10(-94.05)+4(-68.32) \end{array}$$

$$\Delta H=H_{products}-H_{reactants}$$

$$-1231.6=\{10(-94.05)+4(-68.32)\}-\{x+0\}$$
$$x=1231.6-940.5-273.28$$
$$x=17.82 \text{ k. cal mole}^{-1}.$$

Hence the heat of formation of naphthalene is 17.82 k. cal.

Problem 3.13. Calculate the standard heat of formation of sucrose. Given that the standard heat of combustion of sucrose is —1348.9 k. cal/mole and the heats of formation of CO_2 and H_2O are —94.05 k. cal mole^{-1} and —68.32 k. cal mole^{-1} respectively.

Solution. The combustion reaction of sucrose is as under:

$$C_{12}H_{22}O_{11}(s)+12O_2(g)=12CO_2(g)+11H_2O(l)$$
$$\triangle H=H_{products}-H_{reactants}$$
$$-1348.9=[12(-94.05)+11(-68.32)]-x$$
$$x=-1880.12+1348.9$$
$$x=-531.22 \text{ k. cal/mole.}$$

Problem 3.14. Calculate the heat of formation of liquid methanol from the following data:

$$C_2H_5OH(l)+3O_2(g)=2CO_2(g)+2H_2O(l)$$
$$\triangle H=-326.70 \text{ k. cal.} \qquad \dots (1)$$
$$C(s)+O_2(g)=CO_2(g) \quad \triangle H_f{}^\circ=-94.05 \text{ k. cal.} \qquad \dots (2)$$
$$H_2(g)+\tfrac{1}{2}O_2(g)=H_2O(l) \quad \triangle H_f{}^\circ=-68.32 \text{ k. cal.} \qquad \dots (3)$$

Solution. Multiply both sides of equation (2) by 2

$$2C(s)+2O_2(g)=2CO_2(g) \quad \Delta H=-188.1 \text{ k. cal.} \qquad \dots (4)$$

Multiply equation (3) by 3

$$3H_2(g)+3/2\ O_2(g)=3H_2O(l) \quad \triangle H=-204.96 \text{ k. cal.} \qquad \dots (5)$$

Add equations (4) and (5) and subtract equation (1)

$$2C(s)+3H_2(g)+7/2\ O_2(g)-3\ O_2(g)-C_2H_5OH(l)$$
$$=2CO_2(g)+3H_2O(l)-2CO_2(g)-3H_2O(l)$$
$$-188.1-204.96+326.7$$
$$\therefore \quad 2C(s)+3\ H_2(g)+1/2O_2(g)=C_2H_5OH(l)$$
$$\triangle H=-66.36 \text{ k. cal.}$$

Hence the heat of formation of liquid ethanol is —66.36 k. cal/mole.

Problem 3.15. The standard heat of formation of water at 25°C is —57.80 k. cal. Calculate the standard heat of formation of water at 100°C. Given that the mean molar heat capacity for hydrogen is 6.93 cal/deg for oxygen it is 7.04 cal/deg and for water, is 18.03 cal/deg.

Solution. Water is formed according to the equation,

$$H_2\ (g)+\tfrac{1}{2}O_2\ (g)=H_2O(l)$$
$$6.92 \qquad \tfrac{1}{2}\times 7.04 \qquad 18.03$$
$$\triangle C_p=18.03-(6.92+3.52)=7.59 \text{ cal.}=7.59\times 10^{-3} \text{ k. cal.}$$

$T_1=273+25=298$ K
$T_2=273+100=373$ K.
$\triangle H_1= -57.80$ k. cal.

Using Kirchhoff's equation

$$\triangle H_2=\triangle H_1+\triangle C_p(T_2-T_1)$$
$$\triangle H_2= -57.80+7.59\times10^{-3}\times(373-298)$$
$$\triangle H_2= -57.80+7.59\times75\times10^{-3}$$
$$\triangle H_2= -57.80+0.567$$
$$\triangle H_2= -57.233 \text{ k. cal.}$$

Hence the standard heat of formation of water at 100°C is—57.233 k. cal.

Problem 3.16. Calculate the heat of reaction

$C_2H_4(g)+H_2(g) =C_2H_6(g)$. Given that

$C_2H_4(g)+3O_2(g)=2CO_2(g)+2H_2O(l)$

$\triangle H= -337.3$ k. cal.

$H_2(g)+\frac{1}{2}O_2(g)=H_2O(l)$ $\triangle H= -68.3$ k. cal.

$C_2H_6(g)+\frac{7}{2}O_2(g)=2CO_2(g)+3H_2O(l)$

$\triangle H= -372.8$ k. cal.

Add equations (1) and (2) and subtract (3) from them.

$C_2H_4(g)+H_2(g)+3\frac{1}{2}O_2(g)-3\frac{1}{3}O_2(g)=$
$2CO_2(g)+3H_2O-2CO_2(g)-3H_2O\ (l)+C_2H_6(g)$
-337.3 k. cal.-68.3 k. cal.$+372.8$ k. cal.

$\therefore$ $C_2H_4(g)+H_2(g)=C_2H_6(g)$

$\triangle H= -32.8$ k. cal.

Problem 3.17. Calculate the heat of formation of NH_3 gas at 100°C. Given that the heat of formation at NH_3 at 25°C is —10.88 k. cal and the mean molar heat capacities of H_2, N_2 and NH_3 are 6.92 cal deg^{-1}, 5.86 cal deg^{-1} and 8.0 cal deg^{-1} respectively.

Solution. Ammonia is formed according to the equation

$$\tfrac{1}{2}N_2\ (g)+\tfrac{3}{2}H_2\ (g)=NH_3\ (g)$$
$$\triangle C_p=8.0-(\tfrac{1}{2}\times5.86+\tfrac{3}{2}\times6.92)=8.00-13.31$$
$$= -5.31\times10^{-3} \text{ k. cal.}$$

Using Kirchhroff's equation

$$\triangle H_{373}= -10.88+(373-298)\ (-5.31\times10^{-3})$$
$$= -10.88-398.25\times10^{-3}$$
$$= -10.98-0.3983= -10.48 \text{ k. cal.}$$

(**Note.** Data are not the literature value in this problem).

Problem 3.18. The heat of neutralization of LiOH and HCl at 25°C is —8.54 k. cal g $equiv^{-1}$. Calculate the heat of ionization of LiOH.

Solution. Let the heat of ionization of LiOH be I.

Heat of neutralization of LiOH = Heat of Ionization + Heat of neutralization of strong base with a strong acid *i.e.*

$$-8.54 = -13.7 + 1$$

$$\therefore \quad I = +5.16 \text{ k. cal.}$$

Hence the heat of ionization of LiOH is 5.16 k. cal g equiv^{-1}.

Problem 3.19. Calculate the heat of formation of benzene from acetylene at 25°C according to the equation

$$3C_2H_2\,(g) \rightarrow C_6H_6\,(l)$$

Given that the heats of combustion for two moles each of benzene and acetylene being $-1580{,}700$ cal and $-620{,}100$ cal respectively.

Solution. Heat of combustion for one mole of benzene
$= -795.35$ k. cal mole^{-1}

Heat of combustion for one mole of acetylene

$$= -310.05 \text{ k. cal mole}^{-1}$$

The combustion of benzene and acetylene proceeds according to the following equations

$$C_6H_6(l) + 7\tfrac{1}{2}O_2(g) = 6CO_2(g) + 3H_2O(l) - 795.35 \text{ k. cal.} \quad \ldots (1)$$

$$C_2H_2(g) + 2\tfrac{1}{2}O_2(g) = 2CO_2(g) + H_2O(l) - 310.05 \text{ k. cal.} \quad \ldots (2)$$

Multiply equation (2) by 3

$$3C_2H_2(g) + 7\tfrac{1}{2}O_2(g) = 6CO_2(g) + 3H_2O(l) - 930.15 \text{ k. cal.} \quad \ldots (3)$$

subtract equation (3) from equation (1)

$$3C_2H_2(g) = C_6H_6(l) - 134.80 \text{ k. cal.} \quad \ldots (4)$$

Problem 3.20. Calculate the enthalpy of formation of N_2O_5 on the basis of the following data:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad \Delta H(b) = -114.1 \text{ kJ mol}^{-1}$$

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g) \quad \Delta H(a) = -110.2 \text{ kJ mol}^{-1}$$

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H(c) = +180.5 \text{ kJ mol}^{-1}$$

Solution. The above equations may be written as

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g) \quad \Delta H = -110.2 \text{ kJ mol}^{-1}$$

$$2NO(g) + O_2(g) \rightarrow NO_2(g) \quad \Delta H = -114.1 \text{ kJ mol}^{-1}$$

$$2[NO + O_2] + O_2 \rightarrow N_2O_5 \quad \Delta H' = \Delta H + 2\Delta H$$

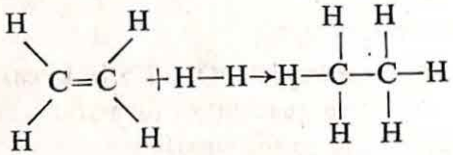
$$N_2 + O_2 \rightarrow 2NO \quad \Delta H = +180.5 \text{ kJ mol}^{-1}$$

$$2[(N_2 + O_2) + O_2] + O_2 \rightarrow 2N_2O_5 \quad \Delta H'' = \Delta H' + \Delta H(c)$$

$$N_2 + \tfrac{5}{2}O_2 \rightarrow N_2O_5 \quad \Delta H_f = \tfrac{1}{2}\Delta H'' = \tfrac{1}{2}[\Delta H(a) + 2\Delta H(b) + 2\Delta H(c)]$$

$$\Delta H_f = \tfrac{1}{2} \times (-110.2 \text{ kJ mol}^{-1}) + (-114.1 \text{ kJ mol}^{-1}) + (180.5 \text{ kJ mol}^{-1}) = 11.30 \text{ kJ mol}^{-1}$$

Problem 3.21. Calculate the heat of reaction at 25°C for the reaction



Given that the bond energy for C—C 80 k. cal, C—H bond is 98.0 k. cal/mole for H—H bond 103 k. cal/mole and for C=C bond energy is 145 k. cal/mole.

Solution.

$\triangle H = H_{reactants} - H_{products}$

Reactants

1 H—H bond=103 k. cal.

1 C=C bond=145 k. cal.

4 C—H bond =392 k. cal.

640 k. cal.

Products

1 C—C bond 80.0

6 C—H bond 588.0

668.0

$\triangle H = 640 - 668 = -28.0$ k. cal/mol.

Problem 3.22. The heats of combustion for *n*-butane, 1 butene and 1, 3 butadiene are —688.0 k. cal, —649.8 k. cal. and —607.9 k. cal respectively. The heat of formation of water is —68.3. Calculate the thermal changes in the reactions.

$$C_4H_{10} \rightarrow C_4H_8 + H_2$$
$$C_4H_{10} \rightarrow C_4H_6 + 2H_2$$

Solution. (1) $C_4H_{10} + 6\frac{1}{2}O_2(g) \rightarrow 4CO_2 + 5H_2O(l)$ -688.0 k. cal.

(2) $C_4H_8 + 6O_2(g) \rightarrow 4CO_2 + 4H_2O(l)$ -649.8 k. cal.

(3) $C_4H_6 + 5\frac{1}{2}O_2(g) \rightarrow 4CO_2 + 3H_2O(l)$ -607.9 k. cal.

(4) $H_2 + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ -68.32 k. cal.

Subtract (2) and (4) from (1)

$\therefore$ $C_4H_{10} \rightarrow C_4H_8 + H_2$ $\triangle H = 30.12$ k. cal.

Multiply (4) by 2 and subtract this and (3) from (1)

$C_4H_{10} \rightarrow C_4H_6 + 2H_2$ $\triangle H = 56.54$ k. cal.

Problem 3.23. Calculate $\triangle H^\circ$ at 25°C from the data given below for the reaction

$$C_{(graphite)} + CO_2(g) \rightarrow 2CO(g)$$

(*i*) $FeO(s) + H_2(g) \rightarrow Fe(s) + H_2O(g)$ $\triangle H^\circ_{25^\circ C} = 5.9$ k. cal.

(*ii*) $Fe(s) + CO_2(g) \rightarrow FeO(s) + CO(g)$ $\triangle H^\circ_{25^\circ C} = 3.9$ k. cal.

(*iii*) $H_2(g)+CO(g) \rightarrow C_{(graphite)}+H_2O(g) \quad \Delta H^\circ_{25^\circ C}=31.4$ k. cal.

Solution. Add (*i*) and (*ii*) and subtract (*iii*) from it.

(*i*) $FeO(s)+H_2(g) \rightarrow Fe(s)+H_2O(g) \quad \Delta H^\circ_{25^\circ C}=5.9$ k. cal.

(*ii*) $Fe(s)+CO_2(g) \rightarrow FeO(s)+CO(g) \quad \Delta H^\circ_{25^\circ C}=3.9$ k. cal.

(*iii*) $H_2(g)+CO(g) \rightarrow C_{(graphite)}+H_2O(g) \quad \Delta H^\circ_{25^\circ C}=-31.4$ k. cal.

$C_{(graphite)}+CO_2(g) \rightarrow 2CO(g) \quad \Delta H^\circ=41.2$ k. cal.

Problem 3.24. Calculate the bond energy of HBr. Given that the heat of formation of HBr, $\Delta H^\circ_f=-36.2$ kJ/mole. Bond energies of H—H and Br—Br are 431 kJ and 188 kJ respectively.

Solution $\frac{1}{2}H_2+\frac{1}{2}Br_2=2HBr \quad \Delta H_{f\ HBr}=-36.2$ kJ

$$\Delta H_{f\,HBr}=\tfrac{1}{2}\text{H—H}+\tfrac{1}{2}\text{Br—Br}-\text{H—Br}$$
$$-36.2=\tfrac{1}{2}\times 431+\tfrac{1}{2}\times 188-\text{HBr}$$

Bond energy of HBr=345.7 kJ.

EXERCISES

3.1. Two moles of hydrogen gas are produced at 25°C and a pressure of 1 atm by the action of acid on a metal. Calculate the work in calories done by the gas in pushing back the atmosphere. [**Ans.** —1184 cal.]

3.2. For an ideal gas derive the equation, for the work done

$$W=C_vT_1\left\{1-\left(\frac{P_2}{P_1}\right)^{R/C_p}\right\}$$

in an reversible adiabatic expansion of 1 mole.

3.3. For each of the following systems determine ΔE, q, and W.

(*a*) A perfect gas changing volume at constant temperature.

(*b*) One mole of liquid being converted into one mole of gas at the boiling point of the liquid.

(*c*) A perfect gas expanding into vacuum.

[**Ans.** (*a*) $\Delta E=0$, $q\neq -w$; (*b*) $\Delta E\neq 0$, $q\neq -w$; (*c*) $\Delta E=q=-w=0$]

3.4. The internal energy of an ideal gas depends only on its temperature. A sample of an ideal gas is allowed to expand isothermally.

(*a*) Does the gas do work?

(*b*) Does the system exchange heat with the surroundings?

(*c*) What happens to the internal energy of the gas?

(*d*) What happens to the temperature of the gas?

[**Ans.** (*a*) yes, (*b*) yes, (*c*) $\Delta U=0$, (*d*) decrease]

3.5. Calculate the work done when 2 moles of water are vaporised against a constant pressure of 3 atm. The temperature is 25°C.

[**Ans.** $W=-1186$ cal.]

3.6. Calculate q, w, ΔH and ΔE for the adiabatic and reversible comparison of one mole of monoatomic ideal gas from 0.1000 m^3 and 25°C to 0.0100 cm^3. [**Ans.** $q=0$, $w=13.6$ kJ; $\Delta E=-13.6$ kJ; $\Delta H=22.6$ kJ.]

3.7. Consider the reversible isothermal expansion of a mole of steam from 1.00 dm^3 to 10.00 dm^3 at 500°C. Calculate the work done assuming (*i*) the gas to be ideal and (*ii*) the gas to obey van der Waals equation.

[**Ans.** (*i*) 14.80 kJ; (*ii*) 14.48 kJ.]

3.8. A steel cylinder of 4 litres capacity contains 20 moles of helium at 25°C. A leak in the valve allows the gas to escape but so slowly that the temperature remains constant. Calculate how much heat must have been absorbed from the surroundings when the cylinder gauge reads empty.
[**Ans.** 57.0 k. cal.]

3.9. Calculate ΔE and ΔH in calories when 2 moles of mercury are heated from 0° to 100°C at 1 atm pressure. The mean density of mercury is 13.474g cm^{-3}, the mean heat capacity 6.69 cal $mole^{-1}$ deg^{-1}, the mean cubical coefficient of expansion 0.182×10^{-3} deg^{-1}.
[**Ans.** $\Delta E = 1337$ cal. $\Delta H = 1338$ cal.]

3.10. If 1000 cal of heat is added to a system while the system does work equivalent to 500 ml by expanding against the surrounding atmosphere, what is the value of ΔE for the system? [**Ans.** +500 cal.]

3.11. One mole of CO gas is expanded adiabatically and reversibly from a volume of 0.38 litres at 25°C to a final volume of 16 litres. What is the final temperature of the gas? Assume the gas to be ideal with $C_v = 5/2\ R$.
[**Ans.** 66.8K]

3.12. Calculate in calories (*a*) *W*, (*b*) ΔE, and (*c*) *Q* for the isobaric expansion at 1 atm pressure of 1 mole of an ideal gas ($C_v = 3/2\ R$, $C_p = 5/3\ R$) from a volume of 20.0 to 30.0 litres.

3.13. Two litres of N_2 at 0°C and 5 atm are expanded isothermally against a constant pressure of 1 atm until the pressure of the gas is also 1 atm. Assuming the gas to be ideal, calculate the values of *W*, ΔE, ΔH and *q* for the pressure. [**Ans.** $W = q = 194$ cal. $\Delta E = \Delta H = 0$.]

3.14. Calculate the change in internal energy when 2.0 g of ethanol are evaporated at the normal boiling point. The specific heat of vaporation of ethanol is 857.7 Jg^{-1}, the specific volume of the ethanol vapour is 607 cm^3 g^{-1}. Neglect the volume of the liquid. [**Ans.** 15.82 kJ.]

3.15. One mole of nitrogen is heated from 0 to 110°C under a pressure of 2 atm. Calculate (*i*) the change in enthalpy; (*ii*) the change in internal energy on the assumption that nitrogen behaves like an ideal gas. The mean specific heat of nitrogen at constant pressure is 1.021 JK^{-1} g^{-1}.
[**Ans.** (*i*) 3146.4 J; (*ii*) 2225.9 J.]

3.16. A steel bottle contains 20 litres of hydrogen at 27°C and a pressure of 50 atm. The gas expands isothermally and reversibly to 100 litres. Calculate (*i*) how much heat had to be supplied; (*ii*) the pressure of the hydrogen after expansion; (*iii*) how much work was performed by the gas during expansion. [**Ans.** (*i*) 162.63 kJ; (*ii*) 10 atm; (*iii*) −163.60 kJ.]

3.17. A gas obeys the van der Waals equation with a 16.69 atm $litre^2/mole^2$ and $b = 0.057$ litre. For gas $C_v = 7.00$ cal deg^{-1} $mole^{-1}$. What will be ΔE for a process involving the compression of 6 moles of the gas from a volume of 100 litres to a volume of 10 litres at 400K. [**Ans.** $\Delta E = 3140$ cal.]

3.18. Calculate the work done in expanding 16 g of oxygen at 27°C and occupying a volume of 5 litres isothermally until the volume becomes 25 litres.
[**Ans.** 2.01×10^3 J.]

3.19. What is the maximum work which can be obtained by the isothermal expansion of 1 mole of an ideal gas at 0°C from 2.24 litres to 22 4 litres?
[**Ans.** 1258 cal.]

3.20. An ideal gas undergoes a compression under a constant pressure of 2.58 atm from 30.01 to 7.91 and evolves 293 J in so doing. Calculate (*i*) work done, (*ii*) the change in internal energy. [**Ans.** (*i*) —5.78 kJ; (*ii*) 5.48 kJ.]

3.21. Calculate the work done when 1 mole of a perfect gas expands isothermally and reversibly from a volume of 1 litre to 10 litres.

[**Ans.** 1372.6 cal.]

3.22. Hydrogen gas is expanded reversibly and adiabatically from a volume of 1.43 litres at a pressure of 3 atm and a temperature of 25°C until the volume is 2.86 litres. The heat capacity C_p of hydrogen can be taken to be 6.90 cal/deg mole.

(*a*) Calculate the pressure and temperature of the gas, assumed to be ideal after the expansion.

(*b*) Calculate q, W, $\triangle E$ and $\triangle H$ for the gas.

[**Ans.** (*a*) 1.37 atm, 226K; (*b*) $q=0$, $w=+62.0$, $\triangle E=-620$, $\triangle H=-871$. cal]

3.23. The heat of formation of FeS (α—s) is —22.72 k. cal mole^{-1} at 25°C under isobaric conditions. What is the value of $\triangle E$? The densities of Fe, S and FeS (α–s) at 25°C are 7.86×10^3, 2.07×10^3 and 4.74×10^3 kgm^{-3} respectively. Assume all the reactants and products to be at 1.00 atm.
[**Ans.** $\triangle H=-95.06$ kJ mole^{-1}; $\triangle V=-4.05\times10^{-6}$ m^3 mole^{-1}; $\triangle(PV)=$ —0.41 J; $\triangle E=$ 95.06 kJ mole^{-1}.]

3.24. If $\alpha=1.25\times10^{-3}$ K^{-1} and $\beta=1.07\times10^{-5}$ atm^{-1}, calculate C_p-C_v for CCl_4. The density of CCl_4 is 1.5940×10^3 kgm^{-3} at 25°C. If $C_p=131.8$ Jk^{-1} mole^{-1}. Calculate C_v. [**Ans.** 42.6 J mole^{-1} K^{-1}; 89.8 J mole^{-1} K^{-1}]

3.25. Five moles of a diatomic ideal gas is allowed to expand isothermally at 25°C from 0 0200 to 0.1000 m^3. Calculate q, W, $\triangle E$ and $\triangle H$ if the expansion is performed (*a*) reversibly, and (*b*) isobatically against constant pressure of 1.00 atm.
[**Ans.** (*a*) $\triangle E=\triangle H=0$, $q=W=$ 19.94 kJ; (*b*) $\triangle E=\triangle H=0$, $q=W=8.11$ kJ.]

3.26. Estimate the equipartition values of C_p for each substance in the reaction

$$C_2H_2(g)+H_2O(g)=C_2H_4O_2$$

(**Hint.** Acetylene is a four atom linear molecule)

[**Ans.** 9.6 cal/deg/mole; 13.8 cal/deg/mole.]

3.27. The relationship $C_p-C_v=\dfrac{\alpha^2TV}{\beta}$ holds for any substance in the gaseous, liquid or solid state. $\alpha=\dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p$ is the coefficient of thermal expansion and $\beta=-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p$ is the isothermal compressibility. Show that for an ideal gas the equation reduces to $C_p-C_v=R$.

3.28. For an adiabatic reversible work done by an ideal gas derive the following expressions

$$-W'=P_1V_1\left[1-\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

$$-W'=\frac{P_2V_2}{\gamma-1}\left[1-\left(\frac{V_2}{V_1}\right)^{\gamma-1}\right]$$

3.29. Calculate the heat of formation of carbon disulphide, given that the heats of combustion of carbon disulphide, carbon and sulphur are—265.100 cal.

—94.300 cal and −71 080 cal respectively **[Ans.** 28,640 cal.]

3.30. Calculate the heat of formation of ethyl acetate from ethyl alcohol and acetic acid. Given that the heats of combustion of ethyl alcohol, acetic acid and ethyl acetate are −34,000 cal, —21,000 cal and —55,400 cal. respectively. **[Ans.** +400 cal.]

3.31. Calculate the heat of formation of carbon monoxide from the following data:

$C\ (s)+O_2\ (g)=CO_2\ (g)\quad \Delta H= -94.0$ k. cal.

$2CO\ (g)+O_2\ (g)=2CO_2\ (g)\quad \Delta H= -13.6$ k. cal.

[Ans. −26.07 k. cal.]

3.32. Calculate the heat of formation of ammonia from the following data:

$2NH_3+\frac{3}{2}O_2\ (g)=3H_2O\ (l)+N_2\ (g)+181200$ cal.

$H_2\ (g)+O_2\ (g =H_2O\ (l)+68{,}300$ cal.

[Ans. 94,335 cal.]

3.33. Calculate the heat of formation of CH_4 Given that the heats of formation of CO_2 (g) and H_2O(l) are —94.3 cal and —68.5 k. cal. respectively. **[Ans.** —19.90 k. cal.]

3.34. The heat released on neutralization of CsOH with all strong acids is 13.4 k. cal/mole. The heat released on neutralization of CsOH with HF is 16.4 k. cal/mole. Calculate ΔH of ionization of HF in water. **[Ans.** −3.0 k. cal/mole.]

3.35. Calculate ΔH for the reaction

$$C_2H_5OH(l)+CH_3COOH(l)=CH_3COOC_2H_5(l)+H_2O(l)$$

from the standard enthalpy of combustion of constituents. Determine the accuracy of calculation if the enthalpies of combustion are measured with an accuracy of ±0.1 per cent. The enthalpies of combustion are as follows:

$C_2H_5OH(l)\ (\Delta H)_{298}= -326.66$ k. cal mole^{-1}

$CH_3COOH(l)\ (\Delta H)_{298}= -208.00$ k. cal mole^{-1}

$CH_3COOC_2H_5(l)\ (\Delta H)_{298}= -538.50$ k. cal mole^{-1}

[Ans. 16 07 kJ, ±13 per cent.]

3.36. Magnetite (Fe_3O_4) is reduced to iron (*i*) by hydrogen, (*ii*) by carbon monoxide. Calculate the change in enthalpy accompanying the reduction of 1 g of iron. Data are given below:

$Fe_3O_4(s)\ (\Delta H)_{298}= -267.00$ k. cal mole^{-1}

$CO(g)\ (\Delta H)_{298}= -26.417$ k. cal mole^{-1}

$H_2O(g)\ (\Delta H)_{298}= -57.798$ k. cal mole^{-1}

$CO_2(g)\ (\Delta H)_{298}= -94.052$ k. cal mole^{-1}.

[Ans. (*i*) 894.1 J; (*ii*) —83.68 J.]

3.37. For butane, $C_4H_{10}(g)$, the standard enthalpy of combustion at 25°C is —2977 kJ/mole. What is ΔE for this reaction at 25°C? **[Ans.** —2868 kJ.]

3.38. Using Hess's law, calculate the average Xe –F bond energy from the following data:

$XeF_4 \rightarrow Xe+F^-+F_2+F\quad \Delta H=1195$ kJ/mole

$Xe \rightarrow Xe+e^-\quad \Delta H=1171$ kJ/mole

$F+e \rightarrow F^-\quad \Delta H=-357$ kJ/mole

$F_2 \rightarrow 2F\quad \Delta H=159$ kJ/mole.

Assume all species to be in the gaseous state and that all data were obtained at the same temperature. **[Ans.** 135 kJ.]

3.39. Calculate ΔH (reaction) for

(a) $N_2+3H_2 \rightarrow 2NH_3$

(b) $H_2O+Cl_2 \rightarrow 2HCl+O_2$

(c) $2HI+Br_2 \rightarrow HBr+I_2$

[**Ans.** (a) —18 k. cal; (b) 13 k. cal; (c) −23 k. cal.]

3.40. A very important organic chemistry reaction is the chlorination of ethylene to form 1, 2 dichloroethane, $C_2H_4(g)+Cl_2(g) \rightarrow C_2H_4Cl_2(l)$. The heat of reaction is −52.2 k. cal/mole. Find the heat of formation of $C_2H_4Cl_2(l)$.

[**Ans.** —39.7 k. cal.]

3.41. Fortunately for inhabitants of our planet, the following reaction is endothermic with a heat of reaction of +89.2 k. cal:

$$CO_2(g)+\tfrac{1}{2}N_2(g) \rightarrow CO(g)+NO(g)$$

Calculate the heat of formation of NO(g). [**Ans.** +21.5 k. cal.]

3.42. Using a known reaction, the heat capacity of a calorimeter is found to be 1.54 k. cal per °C. When 1.04 g of chromium metal, Cr is oxidised to $Cr_2O_3(s)$ in the calorimeter, the temperature increases from 26.0°C to 26.75°C. Find the heat of formation of $Cr_2O_3(s)$ in k. cal. per mole.

[**Ans.** —270 k. cal. mole^{-1}.]

3.43. The molar heat of combustion of naphthalene ($C_{10}H_8$) is —1228.2 k. cal/mole. If 0.2 g of naphthalene burned in a calorimeter raises its temperature by 2.050°C. what is the total heat capacity of calorimeter?

[**Ans.** 1402 cal/°C.]

3.44. The heats of the following reactions at 25°C are

$Na(s)+\tfrac{1}{2}Cl(g)=NaCl(s)$ $\Delta H^\circ = -98{,}230$ cal.

$H_2(g)+S(s)+2O_2(g)=H_2SO_4(l)$ $\Delta H^\circ = -193{,}910$ cal.

$2Na(s)+S(s)+2O_2(g)=Na_2SO_4(s)$ $\Delta H^\circ = -330{,}500$ cal.

$\tfrac{1}{2}H_2(g)+\tfrac{1}{2}Cl_2(g)=HCl(g)$ $\Delta H^\circ = -22{,}060$ cal.

Using the above data, calculate the heat of reaction at constant volume at 25°C for the following reaction,

$2NaCl(s)+H_2SO_4(l)=Na_2SO_4(s)+2HCl(g)$ [**Ans.** 14,560 cal.]

3.45. Calculate the heat of reaction for the process

$$C_2H_4(g)+HCl(g)=C_2H_5Cl(g)$$

given that the heats of formation of C_2H_5Cl, HCl and C_2H_4 are −26.81, −22.062 and 12.49 k. cal. mole^{-1} respectively at 25°C. [**Ans.**—72.13 k cal.]

3.46. Calculate the standard heat of formation of dilute solution of HNO_3 from nitrogen, oxygen and water from the following data.

$HNO_3(9)+NH_3(g) \rightarrow NH_4NO_3$ (aq) $\Delta H = -20.84$ k cal.

$NH_4NO_3+aq. \rightarrow NH_4NO_3(aq.)$ $\Delta H = +6.32$ k. cal.

$NH_4NO_3 \rightarrow N_2(g)+2H_2O(l)+O_2$ $\Delta H = -49.45$ k. cal.

$\tfrac{1}{2}N_2(g)+\tfrac{3}{2}H_2(g) \rightarrow NH_3(g)$ $\Delta H = -16.01$ k. cal.

$H_2(g)+\tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H = -68.35$ k. cal.

[**Ans.** —49.03 k. cal.]

3.47. Find the heat of combustion of nitric oxide from the following data:

$N_2(g)+\tfrac{1}{2}O_2(g) \rightarrow NO(g)$ $\Delta H = +21.6$ k. cal.

$N_2(g)+O_2(g) \rightarrow NO_2(g)$ $\Delta H = +8.1$ k. cal

[**Ans.** −13.5 k. cal.]

3.48. Heats of combustion of *n*-butane, isobutane are —688.0 and −686.8 k. calories respectively at 25°C. Calculate the heat of isomerization of *n*-butane to isobutane at 25°C. [**Ans.** −1.2 k. cal.]

3.49. On igniting 0.1 g of liquid benzene in calorimeter whose water equivalent is 375 g of water and temperature rise of 2.67°C was noted. Calculate the molar heat of combustion of benzene. The specific heat of water is 0.999 cal/g per degree. [Ans. 780 k. cal.]

3.50. The heats of solution of Na_2SO_4, $Na_2SO_4.H_2O$ and $Na_2SO_4.\ 10H_2O$ are 460, −1900 and −18700 calories respectively. What are the heats of hydration of Na_2SO_4 to decalhydrate? [Ans. 19,330 cal.]

3.51. Combustion of diborane proceeds according to the reaction

$$B_2H_6(g)+3O_2(g)\rightarrow B_2O_3(g)+3H_2O(g)$$

and 464 k. cal. are liberated per mole of B_2H_6.
Combustion of boron metal also proceeds to the product B_2O_3 and liberates 283 k. cal./mole of boron used. Calculate the enthalpy change for the reaction

$$2B(s)+3H_2(g)\rightarrow B_2H_6(g).$$

Given that the heat of formation of gaseous water

$\Delta H=-58.0$ k. cal. mole^{-1}. [Ans. —276 k. cal.]

3.52. The enthalpies of formation for SO_2 and NO_2 are —71.0 k. cal./mole and +8.1 k. cal./mole, respectively. Which compound is more stable with respect to the elements? Why? [Ans. SO_2.]

3.53. What is the enthalpy change at 25°C for the following reaction?

$$2N_2O+3O_2\rightarrow N_2O_4$$

Given $\Delta^\circ H_f=19.5$ k. cal. mole^{-1} for N_2O and $\Delta^\circ H_f=2.3$ k. cal. mole^{-1} for N_2O_4. [Ans. −24.4 k. cal.]

3.54. The standard enthalpy of formation of carbon dioxide is expressed as a function of temperature as follows:

$$(\Delta H_f^\circ)_T=93{,}580-0.603T—0.675\times10^{-4}T^2—1.001\times10^5T^{-1}\text{ cal. mole}^{-1}.$$

Find ΔC_p as a function of temperature for this reaction.

[Ans. $\Delta C_p=—0.603—1.350\times T^{-4}+1.001\times10^5T^{-2}$.]

3.55. Calculate the enthalpy of formation for $C_2H_6(g)$ from the following data:

$2C_2H_6(g)+7O_2(g)\rightarrow 4CO_2(g)+6H_2O(l)$ $\Delta H=—3116$ kJ.
$C(s)+O_2(g)\rightarrow CO_2(g)$ $\Delta H^\circ_f=-394$ kJ.
$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l)$ $\Delta H^\circ_f=-285$ kJ.

3.56. At its normal boiling point Br_2 requires 192 J/g to vaporise one mole of the liquid. Calculate ΔH_{vap} and ΔE_{vap}.

[Ans. $\Delta H_{\text{vap}}=30.7$ kJ mole; $\Delta E_{\text{vap}}=28.3$ kJ.]

3.57. The "heat of total cracking" H_{T_c} for a hydrocarbon is defined, for the purpose of this question, as the ΔH_{298K} for a reaction of the type

$$C_nHm+(2n-m/2)\ H_2(g)=nCH_4(g)$$

Given that H_{T_c} is —15.6 cal. for $C_2H_6(g)$ and −20.9 k. cal. for C_3H_8 (g), and that the heat of formation of $CH_4(g)$ at 25°C is —17.9 k. cal, calculate ΔH_{298K} for $CH_4(g)+C_3H_8(g)=2C_2H_6(g)$. [Ans. 10.3 cal.]

3.58. The heat of formation of $C_2H_5OH(l)$ is—66 k. cal./mole, while the heat of combustion of $CO_2(g)$ and $H_2O(l)$ of the isomeric $CH_3—O—CH_3(g)$ is −348 k. cal./mole. The heat of formation of $H_2O(l)$ is −68 k. cal./mole and the heat of combustion of carbon is $CO_2(g)$ is −94 k. cal./mole. Calculate ΔH_{298K} for the isomerization reaction

$C_2H_5OH(l)=CH_3—O—CH_3(g)$ [Ans. 22 k. cal.]

3.59. Consider the titration of a weak acid such as HCN with a strong base such as NaOH according to the reaction

$$HCN(aq.)+NaOH(aq.)=NaCN(aq.)+H_2O(l)$$

If the heats of formation are −68.3174, −21.2, −112.236 and 25.2 k. cal. mole^{-1} at 25°C for H_2O, NaCN, NaOH and HCN respectively. Calculate ΔH_{298} neutralization and heat of ionization.

[**Ans.** −55.898 kJ, +45.4 kJ.]

3 60. Calculate the heat of dilution, for diluting a solution containing one mole of $AgNO_3$ in 100 moles of water by adding 400 moles of water. The heats of formation are −24.637 and −24.362 k. cal. mole^{-1} for the solution consisting of 100 and 500 moles of water respectively added to one mole of $AgNO_3$ at 25°C. [**Ans.** 1.15 kJ.]

3.61. Sodium carbonate dissolves in a large excess of H_2O with the evolution of 5500 cal of heat per mole at 25°C. Calculate the heat of formation per mole of Na_2CO_3 in a dilute solution. [**Ans.** −275,800 cal./mole.]

6.62. At 18°C the heat of solution of anhydrous $CuSO_4$ in a large volume of water is −15,800 cal/mole, while that of $CuSO_4.H_2O$ is 2750 cal./mole. Calculate the heat of the reaction at 18°C

$$CuSO_4(s)+5H_2O(l)=CuSO_4\ 5H_2O(s)$$

[**Ans.** ΔH=—18,550 cal.]

3 63. Bond energies imply the heat liberated in the formation of bond between gas phase atoms. Calculate the average bond energy of C—H bond from the following thermochemical equations:

$$C_{(graphite)}+2H_2(g)=CH_4(g) \qquad \Delta H=-18 \text{ k.cal.}$$
$$C(g)=C_{(graphite)} \qquad \Delta H=+172 \text{ k. cal.}$$
$$H_2(g)=\ H(g) \qquad \Delta H=+104 \text{ k. cal.}$$

[**Ans.** +99.5 k. cal.]

3.64. Calculate the bond energy for C—I if the enthalpy of formation for $CH_3I(g)$ is 3.1 k. cal. mole^{-1}, 52.095 for H(g), 171.291 for C(g) and 25.535 for I(g). and if the average bond energy for C—H bond is 415.9 k. cal. mole^{-1}. [**Ans.** 216.7 k cal. mole^{-1}.]

3.65. The heats of neutralization (ΔH) of sodium hydroxide and ammonium hydroxide with hydrochloric acid are 13.68 and −12.27 k. cal. per mole respectively. Assuming that ammonium hydroxide is practically undissociated, calculate its heat of dissociation. [**Ans.** 1.41 k. cal.]

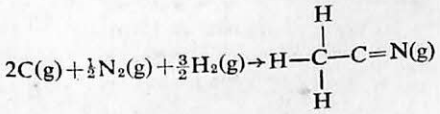
3.66. Saturated solutions of ammonium chloride are often used in sports to reduce the swelling of a sprained ankle. Calculate the temperature drop for

$$NH_4Cl(s)+10H_2O=NH_4Cl\ (\text{in } 10H_2O)$$

if the heat of formation of NH_4Cl (in $10H_2O$) is −71.567 k. cal. mole^{-1} and that of $NH_4Cl(s)$ is −75.15 k. cal. mole^{-1}. The specific heat of solution is 3.77 kJ kg^{-1} K^{-1}.

[**Ans.** ΔH=14.99 kJ; C=0.881 kJ mole^{-1}K^{-1}; 17°C.]

3.67. Calculate the C≡N bond energy $\in_{C\equiv N}$ if the enthalpy change for the reaction



$$2C(g)+\tfrac{1}{2}N_2(g)+\tfrac{3}{2}H_2(g)\rightarrow H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-C\equiv N(g)$$

is

$$\Delta H = -322 \text{ k. cal. mole}^{-1}$$
$$\in_{N \equiv N} = 225 \text{ k. cal. mole}^{-1}$$
$$\in_{H-H} = 103 \text{ k. cal. mole}^{-1}$$
$$\in_{C-C} = 80 \text{ k. cal. mole}^{-1}$$
$$\in_{C-H} = 99 \text{ k. cal. mole}^{-1}$$

[**Ans.** 212 k. cal. mole^{-1}]

3.68. Estimate the enthalpy change for the reaction

$$SiH_4(g) + 4\,HCl(g) \rightarrow SiCl_4(g) + 4H_2(g)$$

Given the bond energies are

$$\in_{S-H} = 76 \text{ k. cal. mole}^{-1}$$
$$\in_{H-Cl} = 103 \text{ k. cal. mole}^{-1}$$
$$\in_{Si-Cl} = 87 \text{ k. cal. mole}^{-1}$$
$$\in_{H-H} = 103 \text{ k. cal. mole}^{-1}.$$

[**Ans.** -44.0 k. cal.]

3.69. Calculate HBr bond energy if

$$\Delta H^\circ_{f\,HBr} = -36.2 \text{ kJ/mole}$$
$$H_2 \rightarrow 2H \qquad \Delta H = 431 \text{ kJ}$$
$$Br_2 \rightarrow 2Br \qquad \Delta H = 188 \text{ kJ}.$$

[**Ans.** 346 kJ.]

4

CHEMICAL THERMODYNAMICS—II

Reversible process. A process is being carried out reversibly when an infinitesimal change in the value of a variable can cause the process to proceed in one direction or the other.

The pressure-volume work in a reversible process is greater than the work that could be done in any other expansion process that allows the gas to undergo the same volume change. The work done in any reversible process is the maximum work obtainable from that process. One important observation in case of reversible process is:

"All the processes that proceed spontaneously from a given initial state to a given final state do so with an increase in randomness."

This is one form of the important generalization called **second law of thermodynamics.** Another form of second law of thermodynamics may be stated as under:

"Heat cannot be completely converted into an equivalent amount of work without causing other changes in some part of the system or its surroundings." This is the statement of second law of thermodynamics.

Efficiency of a Carnot cycle. A Carnot engine is an idealized heat engine that follows the cyclic process. It consists of four steps performed on an ideal gas as shown in Fig. 4.1.

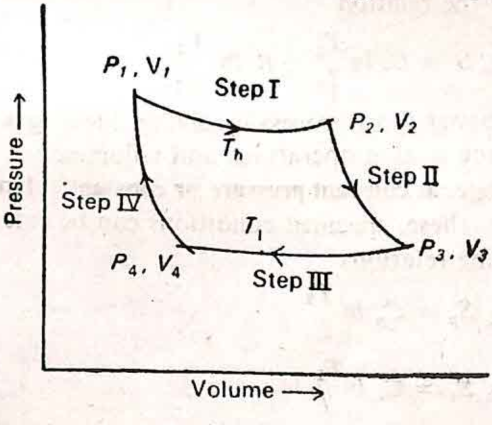


Fig. 4.1

Step I. A reversible isothermal expansion from volume V_1 to V_2 at a temperature T_h.

Step II. A reversible adiabatic expansion from volume V_2 to V_3 with a temperature change from T_h to T_l.

Step III. A reversible isothermal compression from V_3 to V_4 at T_l.

Step IV. A reversible adiabatic compression from V_4 to V_1 at a temperature change from T_l to T_h.

The performance of an engine is usually computed on the basis of the network produced for a given consumption of heat from the hot reservoir. The efficiency, η of a Carnot cycle is given by

$$\eta = \frac{W}{q_h} = \frac{T_h - T_l}{T_h} \qquad \ldots (1)$$

where W is amount of work done and q_h is the amount of heat taken from the hot reservoir. T_h is the temperature of the hot reservoir and T_l is the temperature of the cold reservoir.

Entropy

The entropy change of a reversible process occurring at a temperature T is the defined as

$$\triangle S = \frac{dq}{T} \qquad \ldots (2)$$

The entropy is a Greek word which means change. It is convenient to measure the change in entropy accompanying a particular process. It has the unit cal. deg^{-1} or e.u. (entropy unit).

Entropy changes for an ideal gas. The entropy change for an ideal gas is given by the relation

$$\triangle S = C_v \, ln \, \frac{T_2}{T_1} + R \, ln \, \frac{V_2}{V_1} \qquad \ldots (3)$$

The entropy change for a process involving ideal gas thus depends on the initial and final temperatures and volumes.

Entropy changes at constant pressure or constant volume. The entropy changes under these specified conditions can be calculated with the help of following relations

$$\triangle S_p = C_p \, ln \frac{T_2}{T} \qquad \ldots (4)$$

$$\triangle S_v = C_v \, ln \frac{T_1}{T} \qquad \ldots (5)$$

The entropy change in an irreversible process is given by,

$$\triangle S = R \, ln \, V_2/V_1 \qquad \ldots (6)$$

The entropy of a gas increases in expansion and decreases in a compression. In an irreversible (spontaneous) process $\triangle S$ is positive.

Third law of thermodynamics. According to this law the entropy content of all perfectly crystalline materials is the same at 0°K.

Free energy. The Gibbs free energy G is defined as

$$G = H - TS \qquad \ldots (7)$$

and the Helmholtz free energy A, is defined as,

$$A = E - TS \qquad \ldots (8)$$

Since it is difficult to calculate the absolute values of G and A, we can calculate the changes in G and A i.e. $\triangle G$ and $\triangle A$

$$\triangle G = \triangle H - \triangle (TS) \qquad \ldots (9)$$

$$\triangle A = \triangle G - \triangle (TS) \qquad \ldots (10)$$

At constant temperature,

$$\triangle G = \triangle H - T\triangle S \qquad \ldots (11)$$

$$\triangle A = \triangle E - T\triangle S \qquad \ldots (12)$$

Clausius and Clapeyron equation. The vapour pressures of all substances increase with increasing temperature

$$ln\,\frac{P_2}{P_1} = \frac{\triangle H_{vap}}{R}\left(\frac{T_2 - T_1}{T_2 T_1}\right) \qquad \ldots (13)$$

$\triangle H_v$ = molar heat of vaporization of a given weight of liquid. P_1 is the pressure at temperature T_1 and P_2 is the pressure at a temperature T_2.

Problem 4.1. Compare the maximum efficiency of reversible engines in which working substances are (*i*) H_2O (*ii*) Hg, the heat sources being at their respective boiling points at 1 atmosphere pressure. The boiling point of H_2O = 100°C and Hg = 357°C. The temperature of the sink is 25°C in each case.

Solution. Efficiency of engine using water as the working substance

$$\eta_{H_2O} = \frac{T_n - T_e}{T_n}$$

$$\eta_{H_2O} = \frac{373 - 298}{373}$$

$$\eta_{H_2O} = \frac{75}{373}$$

$$\eta_{HG} = \frac{T_n - T_e}{T_n}$$

$$\eta_{HG} = \frac{630 - 298}{630}$$

$$\eta_{HG} = \frac{332}{630}$$

$$\frac{\eta_{Hg}}{\eta_{H_2O}}=\frac{332}{630}\Big/\frac{75}{375}$$

$$= 1 : 2.622.$$

Problem 4.2. A heat engine works between 130°C and 42°C. Calculate its efficiency.

Solution. Efficiency $\eta=\frac{T_h-T_e}{T_e}$, T_h is the temperature of the hot reservoir and T_e is the temperature of cold reservoir

$$\eta = \frac{403-315}{403} \qquad T_h = 273+130 = 403\text{K}$$

$$\qquad\qquad\qquad T_e = 273+42 = 315\text{K}$$

$$\eta = \frac{88}{403}\times 100$$

$$\eta = 21.84 \text{ per cent.}$$

Problem 4.3. The boiling point of water at 50 atm is 265°C. Compare theoretical efficiencies of a steam engine operating between 55°C (*i*) boiling point of water at 1 atm, (*ii*) boiling point of water at 50 atm.

Solution. At one atmosphere boiling point of water is 100°C, i.e.

$$T_h = 273+100= 373\text{K}$$

$$T. = 273+35 = 308\text{K}$$

$$\eta_{1atm} = \frac{373-308}{373} = \frac{65}{373}$$

The boiling point of water at 50 atm

$$T_h = 273+265 = 538\text{K}$$

$$T_e = 273+35 = 308\text{K}$$

$$\eta_{50atm} = \frac{538-308}{538} = \frac{230}{538}$$

$$\frac{\eta_{1atm}}{\eta_{50atm}} = \frac{65}{373}\times\frac{538}{230}$$

$$= 0.4077.$$

Problem 4.4. Calculate $\triangle S$ for the reversible isothermal expansion of 2.00 moles of an ideal gas from 10.0 to 12.0 litres at 27°C.

Solution. For an isothermal process involving an ideal gas,

$$\triangle E = O \text{ and } Q = -W$$

$$Q = -W = nRT\, ln\, V_2/V_1$$

$$Q = 2.303\, nRT \log \frac{V_2}{V_1}$$

$$\triangle S = \frac{Q}{T} = 2.303\, nRT \log V_2/V_1$$

$$\triangle S = 2.303\, nR \log \frac{V_2}{V_1}$$

$$\triangle S = 2.303(2)(1.987 \text{ cal. deg}^{-1} \text{ mole}^{-1}) \log \frac{12}{10}$$

$$\triangle S = 0.72 \text{ cal/K.}$$

Problem 4.5. Calculate the entropy change of the universe when 2.0 moles of water at 80°C are mixed adiabatically with 3.0 moles of water at 40°C. The heat capacity of water may be considered to be constant at 18 cal. deg^{-1} mole^{-1} over the temperature range of the process.

Solution. In this case 2 moles of hot water is the system and 3.0 moles of cooler water is the surroundings. The sum of the two entropy changes will be the change for the universe. Let X°C be the final temperature.

Heat lost from the system=Heat gained by the surrounding 2 moles (18 cal. deg^{-1} mole^{-1}) (90°C—X)=3 moles (18 cal. deg^{-1} mole^{-1}) (X—40°C).

$$X = 60°\text{C}$$

or

$$273 + 60 = 333\text{K}$$

$$\triangle S_{system} = 2.303 \; nC_p \times \log \frac{T_2}{T_1}$$

$$\triangle S_{system} = 2.303 \text{ (2.00 moles) (18 cal. deg}^{-1} \text{ mole}^{-1}) \log \frac{333}{313}$$

$$\triangle S_{system} = -3.1 \text{ cal. deg}^{-1}$$

$$\triangle S_{surroundings} = 2.303 \times \text{(3 moles) (18 cal. deg}^{-1} \text{ mole}^{-1}) \log \frac{333}{313}$$

$$= 3.3 \text{ cal. deg}^{-1}.$$

$$\triangle S_{universe} = \triangle S_{system} + \triangle S_{surroundings}$$

$$\triangle S_{universe} = -3.1 + 3.3$$

$$\triangle S_{universe} = 0.2 \text{ cal. deg}^{-1}.$$

Problem 4.6. One mole of liquid water at 100°C is placed in a thermostat maintained at 25°C. Calculate the entropy change in the process. The molar heat capacity of liquid water is 18 cal. deg^{-1}.

Solution. The entropy of water changes and the thermostat also takes in heat from water at 100°C, hence the entropy changes. The total entropy change is obtained by adding the two.

$$\text{Entropy change of water} \triangle S_1 = 2.303 \; C_p \log \frac{T_2}{T_1}$$

$$\triangle S_1 = 2.303 \times 18 \log \frac{298}{373}$$

$$\triangle S_1 = 41.454 (\log 298 - \log 373)$$

$$\triangle S_1 = -4.042 \text{ cal. deg}^{-1}$$

Change in entropy of the thermostat.

$$\triangle S_2 = \frac{q}{T_1}$$

$$q = 18 \times 1 \times (T_2 - T_1)$$
$$= 18 \times 1 \times (373 - 298)$$
$$= 18 \times 1 \times 75 = 1350 \text{ cal.}$$

$$\triangle S_2 = \frac{1350}{298} = 4.53 \text{ cal./deg.}$$

Net entropy change $= 4.53 - 4.041 = 0.489$ cal. deg^{-1}.

Problem 4.7. One mole of steam is condensed at 100°C and the water is cooled to 0°C and then frozen to ice. Calculate the entropy change of ice. Given that the latent heat of fusion of ice and latent heat of vaporization of water are 80 cal./g and 540 cal./g respectively.

Solution. The process is being carried out in three different steps:

$$\underset{100^\circ\text{C}}{\text{Steam}} \xrightarrow{\text{I}} \underset{\text{at } 100^\circ\text{C}}{\text{Water}} \xrightarrow{\text{II}} \underset{0^\circ\text{C}}{\text{Water}} \xrightarrow{\text{III}} \underset{\text{at } 0^\circ\text{C}}{\text{Ice}}$$

Step I. Steam is converted into water at 100°C. The change in entropy is:

$$\triangle S_1 = q/T$$
$$q = 18 \times 540 \text{ calories}$$
$$T = 373 \text{ K}$$
$$\triangle S_1 = \frac{9720}{373} = 26.06 \text{ e.u.}$$

Step II. Water at 100°C is brought to 0°C. The change in entropy $\triangle S_2 = 2.303\ C_p \log T_2/T_1$.

$$\triangle S_2 = 2.303 \times 18 \log \frac{273}{373}$$
$$= -5.614 \text{ e.u.}$$

Step III. Water at 0°C is being converted into ice at 0°C. The change in entropy $\triangle S_3$

$$\triangle S_3 = q/T$$
$$q = 18 \times 80 \text{ calories} \qquad T = 273 \text{ K}$$
$$\triangle S_3 = \frac{1440}{273} = 5.274.$$

The total change of entropy $\triangle S = \triangle S_1 + \triangle S_2 + \triangle S_3$

$$\triangle S = 26.06 - 5.614 + 5.274$$
$$\triangle S = 25.720 \text{ calories/deg.}$$

Problem 4.8. Calculate $\triangle G$ for the isothermal expansion of 2.00 moles of an ideal gas at 25°C from a pressure $P_1 = 1$ atm to $P_2 = 0.100$ atm.

Solution. $\triangle G = nRT\ ln\ \frac{P_2}{P_1}$

$$=2.303\ nRT \log P_2/P_1$$

$$=2.303\ (2 \text{ moles})\ (1.987 \text{ cal. deg}^{-1} \text{ mole}^{-1}) \log \left(\frac{0.100}{1.00}\right)$$

$$\triangle G = -2720 \text{ cal.}$$

Problem 4.9. Calculate $\triangle G_{net}$ for the net reaction of alcoholic fermentation of glucose, which proceeds according to the reaction

$$\text{Glucose} \rightarrow 2 \text{ ethanol} + 2CO_2$$

Given $\triangle G$ of glucose and ethanol in aqueous solution are—917.0 and —181.6 kJ mole^{-1} respectively and $\triangle G$ formation of carbon dioxide as a gas is —394.5kJ mole^{-1}.

Solution. $\triangle G_{net} = (\triangle G_{products}) - (\triangle G_{reactants})$

$$=(2 \times \triangle G_{C_2H_5OH} + 2\ \triangle G_f CO_2)$$

$$-\triangle G_{f_{\text{glucose}}}$$

$$=[(2 \times -181.6) + 2 \times (-394.5)] - 917.0 \text{ kJ mole}^{-1}$$

$$\triangle G_{net} = -235.2 \text{ kJ mole}^{-1}.$$

Problem 4.10. The enthalpy and entropy changes for the reaction C (s) diamond$+O_2 \rightarrow CO_2$ (g) at 25°C and 1 atm are—393.4 kJ and 0.006 k J/k respectively. Is the conversion of diamond to carbon dioxide at room temperature a spontaneous process?

Solution. $\triangle G = \triangle H - T\triangle S$

$$\triangle G = 393.4 - (298)\ (0.006)$$

$$= -395.2 \text{ kJ}$$

Since $\triangle G$ is—ve, the reaction is spontaneous.

Problem 4.11. The hydrolysis of adenosine triphosphate which liberates its terminal phosphate group, is a reaction of great biochemical importance and several attempts have been made to measure the values of $\triangle H$, $\triangle S$ and $\triangle G$ for this reaction at "physiological" temperatures and pH values. In one such determination at 309K and pH 7 in the presence of Mg^{2+} ions, it was calculated that when $\triangle H$ was—20.08 kJ mole^{-1} $\triangle S$ was $+35.21$ kJ K^{-1} mole^{-1}. Calculate the corresponding value of $\triangle G$ of the reaction.

Solution. For a closed system at constant temperature, we have the relation,

$$\triangle G = \triangle H - (T\triangle S)$$

$$\triangle G = ?$$

$$\triangle H = -20080 \text{ J mole}^{-1}$$

$$T = 309 \text{ K}$$

$$\triangle S = +35.21 \text{ kJ mole}^{-1}$$

On substituting these values in the above equation we get,

$$\triangle G = -20080-(309\times 35.21)\ \text{J mole}^{-1}$$
$$= -33.96\ \text{kJ mole}^{-1}.$$

Problem 4.12. Calculate the changes in thermodynamic quantities G, S, H and V for mixing of half a mole of oxygen with half a mole of nitrogen at 25° and 1 atm, assuming that the gases are behaving ideally.

Solution. $\triangle G_{mix} = nRT\,(X_1\ ln\ X_1+X_2\ ln\ X_2)$

$$= (1\ \text{mole})\ (2.303)\ (1.987\ \text{cal K}^{-1}\ \text{mole}^{-1})$$
$$\times (298.15\ \text{K})\ (0.5\ \text{K}\log 0.5+0.5\log 0.5)$$
$$= -410\ \text{cal.}$$

$$\triangle S_{mix} = -\triangle G_{mix}/T$$
$$= -410/298$$
$$= 1.376\ \text{cal. K}^{-1}.$$

$$\triangle H_{mix} = 0.$$
$$\triangle V_{mix} = 0.$$

Problem 4.13. Calculate the standard entropy change and the free energy change when 1 mole of water is formed from its elements at 25°C. The standard entropies of H_2, O_2 and H_2O are 31.21 cal. deg^{-1} mole^{-1}, 49.0 cal. deg^{-1} mole^{-1} and 16.73 cal. deg^{-1} mole^{-1} respectively.

Solution. The formation of water can be symbolized as,

$H_2(g)+\frac{1}{2}\ O_2\ (g) = H_2O\ (l)$

$$\triangle S^\circ_f = S^\circ_{H_2O} - S^\circ_{H_2} - \tfrac{1}{2}S^\circ_{O_2}$$
$$\triangle S^\circ_f = 16.73-31.21-24.50$$
$$\triangle S^\circ_f = -38.98\ \text{cal. deg}^{-1}\ \text{mole}^{-1}.$$
$$\triangle G = \triangle H - T\triangle S$$
$$\triangle G = -68{,}320-298\ (-38.98)$$
$$\triangle G = -56{,}700\ \text{cal. mole}^{-1}.$$

Problem 4.14. For a gas that has the equation of state

$$P\bar{V} = RT-BP+APT$$

where $\bar{V}$ is the molar volume, A and B are constants characteristic of the gas, show that

$$\bar{C}_p-\bar{C}_v = R\left(1+\frac{AP}{R}\right)^2.$$

Solution. We know that

$$\bar{C}_p-\bar{C}_v = T\left(\frac{\partial P}{\partial T}\right)_{\bar{V}}\left(\frac{\partial \bar{V}}{\partial T}\right)_P \qquad \ldots (1)$$

and

$$P = \frac{RT}{\bar{V}-AT+B} \qquad \ldots (2)$$

Differentiate (2) with respect to T at constant volume

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V}-AT+B}+\frac{ART}{(\bar{V}-AT+B)^2}$$

$$= \frac{R\bar{V}-ATR+BR+ATR}{(\bar{V}-AT+B)^2} = \frac{R\,(\bar{V}+B)}{(\bar{V}-AT+B)^2}$$

$$\bar{V} = \frac{RT}{P} + AT-B$$

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{R}{P}+A$$

$$\bar{C}_p-\bar{C}_v = \frac{RT\,(\bar{V}+B)\,(R/P+A)}{(\bar{V}-AT+B)^2}$$

$$\bar{C}_p-\bar{C}_v = \frac{RT^2(R/P+A)^2}{(RT/P)^2} = \frac{P^2}{R}\left(\frac{R}{P}+A\right)^2$$

$$\bar{C}_p-\bar{C}_v = R(1+AP/R)^2$$

Problem 4.15. Prove that

(*a*) $\left(\frac{\partial S}{\partial P}\right)_H = -V/T$

(*b*) $\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_v}{TV\alpha}+\frac{\alpha}{\beta}$

Solution. $\partial H = TdS+VdP$

(*a*) $\left(\frac{\partial S}{\partial P}\right)_H = -V/T.$

(*b*)
$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

$$\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P$$

$$= \left(\frac{\partial P}{\partial T}\right)_V + \frac{C_v}{T}\cdot\frac{1}{V\alpha}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)} = \alpha/\beta$$

$$\left(\frac{\partial S}{\partial V}\right)_P = \alpha/\beta+\frac{C_v}{T.\,V\alpha.}$$

Problem 4.16. For a van der Waals gas

(*a*) Show that

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V-nb}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{V-nb}{(2na/RV^3)\,(V-nb)^2-T}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{n^2a}{V^2}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{V-nb}{(2na/RTV^3)(V-nb)^2-1} + V$$

$$\left(\frac{\partial E}{\partial P}\right)_T = \frac{(V-nb)^2}{(2/V)(V-nb)^2-\left(\frac{V^2RT}{na}\right)}$$

(*b*) Evaluate $\triangle E$, $\triangle H$, $\triangle A$, $\triangle G$ and $\triangle S$ for an isothermal expansion.

Solution. van der Waals equation for *n* moles can be written in the following three forms:

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb) = nRT \qquad \ldots (1)$$

$$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} \qquad \ldots (2)$$

$$PV = \frac{nRT}{(1-nb/V)} - \frac{n^2a}{V} \qquad \ldots (3)$$

(*a*)
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Differentiating equation (1) implicitly,

$$\left(P+\frac{n^2a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P - \frac{n^2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P (V-nb) = nR.$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{(2n^2a/V^3)(V-nb)-(P+n^2a/V^2)}$$

$$= \frac{nR}{(2n^2a/V^3)(V-nb)-nRT\,(V-nb)}$$

$$= \frac{V-nb}{(2na/RV^3)(V-nb)^2-T}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = \frac{n^2a}{V^2}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V = \frac{V-nb}{(2na/RTV^3)(V-nb)^2-1} + V$$

$$\left(\frac{\partial E}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - V - P\left(\frac{\partial V}{\partial P}\right)_T$$

Differentiating equation (1) implicitly,

$$\left[1-\frac{2n^2a}{V^3}\left(\frac{\partial V}{\partial P}\right)_T\right](V-nb) + \left(P+\frac{n^2a}{V^2}\right)\left(\frac{\partial V}{\partial P}\right)_T = 0$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{V-nb}{(2n^2a/V^3)(V-nb) - nRT/(V-nb)}$$

$$= \frac{(V-nb)^2}{nRT\,[(2na/RTV^3)\,(V-nb)^2-1]}$$

$$P\left(\frac{\partial V}{\partial P}\right)_T = \frac{V-nb}{(2na/RTV^3)\,(V-nb)^2-1}$$

$$-\frac{na\,(V-nb)^2}{V^2RT\,[(2na/RTV^3)\,(V-nb)^2-1]}$$

Therefore

$$\left(\frac{\partial E}{\partial P}\right)_T = \frac{(V-nb)^2}{(2/V)\,(V-nb)^2 - V^2RT/na}$$

$$(b) \qquad \triangle E \quad = \int_{V_1}^{V_2} \frac{n^2a}{V^2}\,dV = -n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

$$\triangle H = \triangle E + \triangle(PV)$$

$$\triangle(PV) \quad = nRT\left(\frac{1}{1-nb/V_2}-\frac{1}{1-nb/V_1}\right) - n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

$$\triangle H \quad = 2n^2a\left(\frac{1}{V_1}-\frac{1}{V_2}\right) + nRT\left(\frac{1}{1-nb/V_2}-\frac{1}{1-nb/V_1}\right),$$

$$\triangle A \quad = -\int_{V_1}^{V_2} PdV = -\,nRT\,ln\left(\frac{V_2-nb}{V_1-nb}\right) - n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

$$\triangle G \;=\; \triangle A + \triangle(PV) = -\,nTR\;\;ln\left(\frac{V_2-nb}{V_1-nb}\right)$$

$$-2\,n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right) + nRT\left(\frac{1}{1-nb/V_2}-\frac{1}{1-nb/V_1}\right)$$

$$\triangle S = \int_{V_1}^{V_2}\left(\frac{\partial S}{\partial V}\right)_T dV = nR\,ln\,\frac{V_2-nb}{V_1-nb}\,.$$

Problem 4.17. The boiling point of ether is 33.5°C at 760 mm pressure. At what temperature will it boil at a pressure of 750 mm. Given that the latent heat of vaporization of ether is 88.4 calories per gm and the molecular weight of ether is 74.

Solution. $P_2 = 750$ mm, $T_2 = ?$

$P_1 = 760$ mm, $T_1 = 306.5$ K

$\triangle H_{vap} = 88.4 \times 74$ cal per mole

$$\log\frac{P_1}{P_2} = \frac{\triangle H_{vap}}{R}\left(\frac{T_2-T_1}{T_1\,T_2}\right)$$

$$\log \frac{760}{7650} = \frac{88.4 \times 74\ (T_2 - 306.5)}{2.303 \times 1.987 \times 306.5\ T_2}$$

$$T_2 = 305.9\ \text{K} = 32.9^\circ\text{C}.$$

Problem 4.18. The vapour pressure of liquid *A* is 50 mm Hg at 46°C; this vapour pressure is 0.50 mm greater than that of solid *A* at the same temperature. At 45°C the vapour pressure of liquid is 1.00 mm greater than that of the solid ΔH 9.0 k. cal. (*a*) Estimate the melting point of *A*, (*b*) calculate the heat of fusion and sublimation of *A*.

Solution. $\left(\frac{dP}{dT}\right)_v = \frac{\Delta H \times P}{RT^2} = \frac{9000 \times 50}{1.98 \times 319 \times 319} = 2.2$ mm/deg

At the melting point the liquid and solid must have the same vapour pressure. Since the difference is 1.00 mm at 45°C and 9.5 mm at 46°C, it should be zero at 47°C. Hence the melting point of the solid should be 77°C.

Problem 4.19. What is the change in the boiling point of water at 100° per Torr change in atmospheric pressure? The heat of vaporization is 539.7 cal. g^{-1}, the molar volume of liquid water is 18.78 cm^3, and the molar volume of steam is 30.199 litres, all 100°C and 1 atm.

Solution. $\frac{dP}{dT} = \frac{\Delta H_{vap}}{T\,(V_v - V_l)}$

$$= \frac{(539.2\ \text{cal. g}^{-1})\ (18.02\ \text{g mole})\ (0.0412\ \text{g litre atm cal.}^{-1})}{(373.1\ \text{K})\ (30.180\ \text{litre mole}^{-1})}$$

$$dP/dT = 0.03566\ \text{atm K}^{-1}$$

$$dP/dT = (0.03566\ \text{atm K}^{-1})\ (760\ \text{Torr atm}^{-1})$$

$$dP/dT = 27.10\ \text{Torr K}^{-1}.$$

Problem 4.20. The normal boiling point of chloroform is 344 K. At 328 K, the vapour pressure of chloroform is 0.824 atm. What is the heat of vaporisation of chloroform for this temperature range?

Solution. If we set $T_2 = 344$ K, then $P_2 = 1.00$ atm, $T_1 = 328$ K, $P_1 = 0.824$ atm.

$$\log\left(\frac{P_2}{P_1}\right) = \left(\frac{\Delta H_v}{2.303\ R}\right)\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\left(\frac{1.00\ \text{atm}}{0.824\ \text{atm}}\right) = \left(\frac{\Delta H_v}{(2.303)(8.314\ \text{J/K. mol})}\right) \Big/ \left[\frac{334\ \text{K} - 328\ \text{K}}{(328\ \text{K})\ (334\ \text{K})}\right]$$

$$\Delta H_v = 29{,}390\ \text{J/mol}$$

$$\Delta H_v = 29.4\ \text{kJ/mol}.$$

Problem 4.21. The vapour pressure of carbon disulphide at 301 K is 0.526 atm. What is the vapour pressure of CS_2 at 273 K? The heat of vaporisation over this range of temperature may be taken as 27,6 kJ/mol.

Solution. $T_2 = 301$ K, $P_2 = 0.526$ atm, $T_1 = 275$ K

$$\log\left(\frac{P_2}{P_1}\right) = \left(\frac{\Delta H_v}{2.303\,R}\right)\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\left(\frac{0.526\text{ atm}}{P_1}\right) = \left(\frac{27{,}600\text{ J/mol}}{(2.303)(8.314\text{ J/K mol})}\right)\left[\frac{301\text{ K} - 273\text{ K}}{(273\text{ K})\,(301\text{ K})}\right]$$

$$= 0.491$$

$$\frac{0.526}{P_1} = 3.10$$

$$P_1 = 0.170\text{ atm.}$$

EXERCISES

4.1. Which of the following are extensive quantities? (*a*) energy (*b*) free energy (*c*) entropy (*d*) temperature (*c*) enthalpy. [Ans. (*a*), (*b*), (*c*), (*e*)]

4.2. Which is the best definition of the heat of reaction? (*a*) $\Delta E + P\Delta V$ (*b*) $E + PV$ (*c*) the enthalpy of reaction at constant pressure (*d*) $P\Delta V$ (*e*) $\Delta(PV)$. [Ans. (*c*)]

4.3. The state function which has to be introduced to account for unidirectional changes is (*a*) enthalpy (*b*) entropy (*c*) free energy (*d*) energy (*e*) heat content. [Ans. (*b*)]

4.4. At equilibrium which of the following is zero? (*a*) $T\Delta S_{fus}$ (*b*) ΔS (*c*) ΔS_{fus} (*d*) ΔG (*e*) $\Delta H_{fus.}$? [Ans. (*d*)]

4.5. What is the maximum efficiency of a steam engine operating between 120°C and 20°C? [Ans. 25.4 per cent]

4.6. Calculate thermodynamic efficiency of a heat engine operating between temperatures of (*a*) 0°C and—100°C, (*b*) —100°C and—200°C. [Ans. (*a*) 36.6 per cent, (*b*) 57.8 per cent]

4.7. A bar of metal having a mass of 50 g and a temperature of 100°C is dropped into a beaker containing 100 g of water at 25°C. Determine the final temperature of the system and ΔS_{metal}, ΔS_{H_2O} and $\Delta S_{univ.}$ for the process. Assume that the beaker is completely isolated from surroundings and that the metal has a heat capacity of 0.389 $J.g^{-1}K^{-1}$. The heat capacity of water is 4.18 $J.g^{-1}K^{-1}$.
[Ans. $\Delta S_{H_2O} = +4.60\text{ J K}^{-1}$, $\Delta S_{univ.} = 0.45\text{ JK}^{-1}$]

4.8. Compare the efficiency of a Carnot engine using liquid water as a working fluid at 50 atm pressure with the same engine at 1 atm. Assume that the upper reservoir is at the boiling point of water and the sink is 25°C in each case. The boiling point of water at 50 atm is 265°C. [Ans. 2.22 times as efficient]

4.9. One mole of He at 25°C is compressed isothermally and reversibly from a volume of 10*l* to a volume of 3*l*. Calculate ΔS_g, $\Delta S_{surr.}$ and $\Delta S_{univ.}$ for the process.
[Ans. $\Delta S_g = -10.0\text{ J.K}^{-1}$, $\Delta S_{surr.} = +10.0\text{ J.K}^{-1}$, $\Delta S_{univ.} = 0$]

4.10. Calculate $\Delta S_{\text{univ.}}$ for freezing of 1 mole of water to ice at +10°C. The heat of fusion of ice is 6025 J. mole^{-1} at 273.15 K. [**Ans.** -0.90 J. K^{-1}.]

4.11. Calculate the entropy change involved in the thermodynamic expansion of 2 moles of an ideal gas from a volume of 5 litres to a volume of 50 litres at 30°C.

4.12. Calculate the entropy change when two moles of an ideal gas is heated from a volume of 100 litres at 50°C to a volume of 150 litres at 150°C. (C_v=7.88 cal deg^{-1} mole^{-1}, R=1.987 cal deg^{-1} mole.) [**Ans.** 4.99 e.u.]

4.13. For the melting of sodium chloride heat required is 7.26 k.cal mole^{-1} and the entropy increases to 6.73 cal mole^{-1} deg^{-1}. Calculate the melting point of the salt. [**Ans.** 804°C.]

4.14. Ten grams of helium is compressed isothermally and reversely at 100°C from a pressure of 2 atm to 10 atm. Calculate (*i*) Q, (*ii*) W, (*iii*) ΔH, (*iv*) ΔE, (*v*) ΔS, (*vi*) ΔG. Assume ideal behaviour.

[**Ans.** (*i*) $Q=-2982$ cal, (*ii*) $W=2982$ cal, (*iii*) $\Delta H=0$, (*iv*) $\Delta E=0$, (*v*) $\Delta S=-7.992$ cal deg^{-1}, (*vi*) $\Delta G=2982$ cal.]

4.15. Calculate the free energy of formation of urea $CO(NH_2)_2(s)$ from the following data:

$CO_2(g)+NH_3(g)=H_2O(g)+CO(NH_2)_2(s)$, $\Delta G^\circ_{298}=456{,}1$ cal

$H_2O(g)=H_2(g)+\frac{1}{2}O_2(g)$ $\Delta G^\circ_{298}=54{,}635$ cal

C (graphite)$+O_2(g)=CO_2(g)$ $\Delta G^\circ_{298}=-94{,}260$ cal

$N_2(g)+3H_2(g)=2NH_3(g)$ $\Delta G^\circ_{298}=-7{,}952$ cal

[**Ans.** $\Delta G^\circ_{\text{formation}}=-47{,}121$.]

4.16 The freezing point of benzene at 1 atm pressure is 5.45°C. The density of solid benzene is 0.978 g/c.c. and the density of the liquid is 0.874 g/c.c. at the melting point.

$\Delta H_{\text{fusion}}=2350$ cal/mole for benzene. For the process

C_6H_6 (l, 1 atm, 5.45°C)$\rightarrow C_6H_6$ (s, 1 atm, 5.45°C)

Calculate (*i*) ΔS, (*ii*) W, (*iii*) Q, (*iv*) ΔG.

[**Ans.** (*i*) $\Delta S=-8.435$ cal deg^{-1} mole^{-1}, (*ii*) $W=0.23$ cal mole^{-1}, (*iii*) $Q=-2350$ cal, (*iv*) $\Delta G=0$]

4.17. Calculate the entropy change involved in the conversion of one mole of liquid water at 100°C to vapour at the same temperature. Latent heat of vaporization of water is 540 cal/g. [**Ans.** 26.06 cal.]

4.18. Could the following reactions proceed spontaneously?

(*a*) Malate$^{-2}\rightarrow$fumarate$^{-2}+H_2O$ (298K)

(*b*) lencine+glycine$\rightarrow$lencylglycine$+H_2O$ (298K)

(*c*) Oxaloacetate$^{2-}+H_2O\rightarrow$pyruvate$^{-}+HCO_3^{-}$ (298K)

(*d*) Ice$\rightarrow$water (263K)

Values for the standard Gibbs free energies at 298K in kJ mol^{-1} are as follows:

malate^{-2} −844
fumarate^{-2} −604
Oxaloacetate^{-2} −796
pyruvate^{-} −474
HCO_3^{-} −586

lencine −341
glycine −373
lencylglycine −464
water −237

[**Ans.** (*a*) $\Delta G=+3$ kJ mol^{-1} would not proceed spontaneously. (*b*) $\Delta G=$ 13 kJ mol^{-1} would not proceed spontaneously. (*c*) $\Delta G=-27$ kJ mol^{-1}

would proceed spontaneously, (*d*) would not proceed spontaneously below 273.15 K.]

4.19. Calculate the entropies of vaporisation in cal K^{-1} mol^{-1} of the following substances from their boiling points and enthalpies of vaporisation.

	Boiling Point/K	ΔH_{vap}/k cal mol
C_6H_6	353	7.35
$CHCl_3$	334	7.02
H_2O	373	9.70
C_2H_5OH	351	9.20

In terms of the structures of the liquids suggest reasons for higher values observed for H_2O and C_2H_5OH.

[**Ans.** C_6H_6: 20.8 cal k^{-1} mol^{-1}, $CHCl_3$ 21.0 cal k^{-1} mol^{-1}, H_2O 26.0 cal k^{-1} mol^{-1}, C_2H_5OH 26.2 cal k^{-1} mol^{-1}, Hydrogen bonding in H_2O and C_2H_5 accounts for higher values.]

4.20. Calculate the change in entropy of 5 moles of an ideal gas when a gas is expanded reversibly and isothermally from 2 atm to 1 atm pressure at 25°C. What would be the entropy changes of the system and surroundings if the expansion were performed adiabatically?

[**Ans.** $\Delta S_{gas} = +6.89$ cal/deg.]

4.21. The entropy and enthalpy changes for the reaction $H_2(g)+I_2(s)=2HI(g)$ at 25°C and 1 atm are 51.8 kJ and 0.165 kJ/K, respectively. Is the formation of HI spontaneous at room temperature?

[**Ans.** $\Delta G = +$ve the reaction is not spontaneous.]

4.22. ΔG° for the reaction

$$N_2+3H_2 \rightarrow 2NH_3$$

is -33.26 kJ and ΔH for the reaction—92.36 kJ. Calculate ΔS for the reaction. [**Ans.** -0.198 kJ/K.]

4.23. The enthalpy change for a certain reaction at 298K is -5.0 k. cal/mole. The entropy change under these conditions is -7.2. cal/mole deg. Calculate the free energy change for the reaction. [**Ans.** -2.9 k. cal/mole.]

4 24. Calculate the entropy changes for heating one mole of silver from 298 K to 1500 K at constant pressure if the process is performed (*i*) reversibly, (*ii*) irreversibly by placing the silver in an oven at 1500 K. The average value of C_p for silver is 259 J $mole^{-1}$ K^{-1}. [**Ans.** (*i*) 41.9 e.u. (*ii*) -20.75 e.u.]

4.25. The values of ΔH and ΔS for a chemical reaction are -22.6 k. cal and -45 2 k. cal/deg respectively, and these values are not changed much by temperature changes. Calculate ΔG (*i*) at 300 K, and (*ii*) at 1000 K, for the reaction. [**Ans.** (*i*) -9040 cal, (*ii*) 22,600 cal.]

4.26. The transition point of α-sulphur to β-sulphur is 96°C at one atmospheric pressure. The densities of α-sulphur and β-sulphur at this temperature are 2.03 g cm^{-3} and 1.98 g cm^{-3} respectively. The heat absorbed in the change is 77 cal/per gram atom What is the transition temperature at 10 atm pressure? Given that $g=981$ cm sec^{-2}, density of mercury$=13.6$ g cm^{-3} and 1 cal$=4.2\times10^7$ ergs. [**Ans** 96.418°C]

4.27. The vapour pressure of water at 90°C and 100°C are 526 mm and 760 mm respectively. Calculate the mean heat of vaporization of water between 90°C and 100°C. [**Ans.** 9954 cal $mole^{-1}$.]

4.28. At what temperature will water boil at a space station where the atmospheric pressure is 528 mm of Hg. The latent heat of vaporization of water is 545.5 cal g^{-1}. The boiling point of water is 100°C at 760 mm Hg.
[**Ans.** 90°C.]

4.29. The vapour pressure of water at 25°C is 23.76 mm Hg. What is the vapour pressure at 35°C, given that ΔH_v for water is 40, 360 J $mole^{-1}$?
[**Ans.** 40.43 mm Hg.]

4.30. The heats of vaporization and of fusion of water are 595 cal/g and 79.7 cal/g at 0°C. The vapour pressure of water at 0°C is 4.58 mm. Calculate the sublimation pressure of ice at -15°C, assuming that the entropy changes are independent of temperature. [**Ans.** 1.25 mm.]

4.31. Propane has the following vapour pressures at 150 K, $P=3.28$ mm; at 200K. $p=198.0$ mm; at 250K, $p=2074$ mm at 300K, $p=10{,}040$ mm. From these data calculate (*a*) the heat of vaporization, and (*b*) the vapour pressure at 225K by a graphical method.
[**Ans.** (*a*) 4670 cal/mole, (*b*) 741 mm.]

4.32. What is the boiling point of water on a mountain where the barometer reading is 600 mm? The heat of vaporization of water may be taken to be 9.72 k. cal/mole. [**Ans.** 93°C.]

4.33. The heat of vaporization of ether is 88.39 cal g^{-1} at its boiling point, 34.5°C (*a*) calculate the rate of change of vapour pressure with temperature at the boiling point, (*b*) what is the boiling point at 750 mm? and (*c*) estimate the vapour pressure at 36°C.
[**Ans.** (*a*) 26.5 mm deg^{-1}, (*b*) 34.1°C, (*c*) 800 mm.]

4.34. Gas for use in rescue work could be made as follows. Ten moles of N_2 originally at 50 atm pressure and twenty moles of O_2 originally at 60 atm. of pressure are put into a cylinder in which the final total pressure is 20 atm. Temperature is kept constant at 25°C. Assume the gases to be ideal. Calculate ΔE, ΔH, ΔS, ΔA and ΔG.
[**Ans.** $\Delta E=\Delta H=0$, $\Delta S=100.2$ e.u., $\Delta A=-29.8$ k. cal, $\Delta G=-29.8$ cal.]

4.35. The power of the sun's radiation incident on the earth is approximately 1.2 k W/m^2 on a clear day. If the temperature of a lake stays constant and all the cooling is by evaporation, how much is the water level lowered in 12 hours? The heat of vaporization is 540 cal/g. [**Ans.** 2.3 cm.]

4.36. For nitromethane at 15K, the molar heat capacity is 0.89 cal/deg mole. Assume the Debye T^3 law holds for temperatures below 15K, calculate the molar entropy at 15K and the molar enthalpy relative to its value at 0 K
[**Ans.** $S=0.30$ e.u./mole, $H-H$ (0K)$=3.34$ cal/mole.]

4.37. A gas obeys the equation of state: $pV=nRT+nbp$, where b is a constant. If n moles of the gas expand from V_1 to V_2 reversibly at constant temperature T, calculate (*a*) ΔA, (*b*) ΔG, (*c*) ΔS, (*d*) ΔE, (*e*) W, and (*f*) Q.
[**Ans.** (*a*) $-nRT\ ln\ [(V_2-nb)/(V_1-nb)]$; (*b*) $nRT\ (V_2/(V_2-nb)-V_1/V_1-nb)]$ $-nRT\ ln\ [(V_2-nb)/(V_1-nb)]$; (*c*) $nR\ ln\ [(V_2-nb)/(V_1-nb)]$; (*d*) 0; (*e*) $-nRT\ ln\ [(V_2-nb)/(V_1-nb)]$; (*f*) $+nRT\ ln\ [(V_2-nb)\ (V_1-nb).]$

4.38. Ten grams of water at 20°C is mixed with 10 g water at 80°C in an insulated vessel. Calculate W, Q, ΔE, ΔH, ΔS, ΔA and ΔG. The molar entropy of water is 18.17 e.u. at 50°C.
[**Ans.** $W=0$, $Q=0$, $\Delta H=0$, $\Delta S=0.094$ e.u., $\Delta A=26$ cal, $\Delta G=26$ cal.]

4.39. The following absolute molar entropies are given at 25°C, for H_2 (g), 31.211

e.u.; for $Cl_2(g)$ 63.286 e.u.; for HCl(g) 44.617 e.u. What is the molar entropy of formation of HCl(g) from $H_2(g)$ and $Cl_2(g)$ at 25°C? What is $\triangle S$ for the reaction $2HCl(g)=H_2(g)+Cl_2(g)$?

[**Ans.** 2.368 e.u., −4.737 e.u.]

4.40. A thermostat was maintained at a temperature of 96.9°C. The air in the room was at 26.9°C. During a certain length of time 1000 cal of heat leaked through the thermostat insulation into the room. (*a*) What was the entropy change of the material in the thermostat? (*b*) What was the entropy change of the air in the room? (*c*) Was the process reversible or irreversible?

[Ans. (*a*) −2.70, (*b*) 3.33 cal deg^{-1}; (*c*) entropy change=0.63 cal deg^{-1}, therefore the process is irreversible.]

4.41. It has been determined that the free energy of formation of $H_2O(g)$ is −54.6 k. cal per mole and the free energy of formation of liquid water is −56.7 k. cal per mole at 25°C and 1 atm pressure. Calculate the entropy change, $\triangle S$, for the vaporization of water at 25°C and 1 atm.

(**Ans.** 0.0285 k. cal/K.)

4.42. At 1 atm pressure silicon tetrachloride melts at a temperature of −68°C and boils at a temperature of 57°C. For the phase change from solid to liquid, $\triangle H$ is 1840 cal $mole^{-1}$. For the phase change from liquid to gas, $\triangle H$ is 6140 cal $mole^{-1}$. Calculate $\triangle S$ at 1 atm for the reaction

$SiCl_4(s)—SiCl_4(l)$ at −68°C. [**Ans.** 9.0 cal $mole^{-1}K$.]

4.43. Would you expect $\triangle S$ to be positive, negative or near zero for the following:

(*i*) Universe expands,
(*ii*) Water freezes,
(*iii*) A leaf forms on a tree,
(*iv*) A crystal melts.

[**Ans.** (*i*) positive, (*ii*) negative, (*iii*) negative, (*iv*) positive.]

4.44. Indicate whether there is an increase or decrease of entropy in each of the following:

(*i*) Sugar dissolves in water.
(*ii*) A dozen marbles are taken out of a small bag and dropped on the ground.
(*iii*) Evaporation of water.
(*iv*) A given quantity of CO_2 gas is changed into dry ice.
(*v*) Carbon dioxide gas is forced into bottles during the process of carbonation.
(*vi*) Three atoms combine to form a single molecule.

[**Ans.** (*i*) increases, (*ii*) increases, (*iii*) increases, (*iv*) decreases, (*v*) decreases, (*vi*) decerases.]

5

SOLUTIONS

INTRODUCTION

A number of chemical reactions occur in the gas phase, and a few take place in the solid state, but a very large number of reactions take place in solution. A solution is defined as a homogeneous mixture of two or more components. Since they are mixtures, solutions have properties which depend on the properties of their constituents and on the relative quantities of each of the constituents present.

It is customary and convenient to regard one constituent of the solution as the solvent and the other as solute.

Gases mix readily with one another in any proportion to form gas phase solutions. Some pairs of liquids, such as water and ethyl alcohol, also form solution regardless of the proportions of the constituents. A general rule often useful for predicting solubilities in terms of molecular structure is "like dissolves like." Solvents having molecules with dipole moments, such as water dissolve solutes with dipolar molecules and solutes which are ionic. Solvents having molecules without dipoles dissolve solutes of similar nature. Thus carbon tetrachloride dissolves hydrocarbons, iodine and other nonpolar materials, which generally are insoluble in water.

Henry's Law

It has been observed that the solubility of gases, decreases with increasing temperature. At a given temperature, the solubilities of gases, which do not react extensively with the solvent, are directly proportional to the partial pressures of the gases above the solution. This proportionality is known as Henry's law. Mathematically, it may be expressed as,

$$[X]=KP_x \qquad \ldots (1)$$

where $[X]$ is the concentration of the dissolved gas, P_x is its partial pressure above the solution.

Raoult's Law

In a solution, the properties of the solvent, such as its vapour pressure and the boiling point are modified by the presence of a solute. The modification depends on the relative numbers of solute and solvent molecules.

A hypothetical ideal solution is defined as one which can be formed from its components with no evolution or absorption of heat and whose volume is the sum of the volumes of individual constituents. The vapour pressure P_A of a volatile component, A, of such a solution is proportional to its mole fraction. The proportionality constant is simply the vapour pressure of the pure component, P°_A at the same temperature

$$P_A = N_A P^\circ_A \qquad \ldots (2)$$

This relationship is known as Raoult's law.

Steam Distillation

If two constituents of an ideal solution are volatile, the vapour pressure of each will be lowered in accordance with Raoult's law. For two such substances A and B, at a given temperature,

$$P_A = N_A P^\circ_A \qquad \ldots (3)$$

$$P_B = N_B P^\circ_B \qquad \ldots (4)$$

The vapour pressure of the solution is the sum of the vapour pressure of the two constituents;

$$\begin{aligned} P_{\text{solution}} &= P_A + P_B \\ &= N_A P^\circ_A + N_B P^\circ_B \qquad \ldots (5) \end{aligned}$$

P°_A and P°_B are the vapour pressures of the pure liquids A and B respectively, at the given temperature. N_A and N_B are the numbers of moles of each present in the vapour. The composition of the vapour is given by

$$\frac{N_A}{N_B} = \frac{P^\circ_A}{P^\circ_B} \qquad \ldots (6)$$

To express the ratio of A to B in the vapour in terms of the actual weights W_A and W_B, the numbers of moles must be multiplied by the respective molecular weights M_A and M_B

$$\frac{W_A}{W_B} = \frac{n'_A}{n'_B}\frac{M_A}{M_B}$$

$$\frac{W_A}{W_B} = \frac{P^\circ_A M_A}{P^\circ_B M_B} \qquad \ldots (7)$$

A system of two immiscible liquids will distil when the total vapour pressure P is equal to the atmospheric pressure. The boiling point of the mixture is thus lower than that of either of the constituents.

Problem 5.1. How many grams of NaOH are required to prepare (*a*) 500 ml of a 0.04 M solution, and (*b*) 250 ml of a dilute NaOH solution of pH 9.7?

Solution. (*a*) Number of moles of NaOH required = litres × M

0.02 mole NaOH required $= 0.5 \times 0.04$

$$\text{Number of moles} = \frac{\text{Weight in grams}}{\text{Molecular Weight}}$$

$$0.02 = \frac{\text{Weight in grams}}{40}$$

$$\text{Weigh in grams} = 0.02 \times 40$$
$$= 0.8 \text{ g.}$$

Weigh out 0.8 g, dissolve in water and dilute to 500 ml.

(*b*)
$$\text{pH} = 9.7$$
$$\text{pH} = \log \frac{1}{[H^+]}$$
$$9.7 = \log \frac{1}{[H^+]}$$
$$\frac{1}{[H^+]} = \text{antilog } 9.7$$
$$[H^+] = 0.2 \times 10^{-9}$$
$$= 2.0 \times 10^{-10}\text{M}$$
$$[H^+][OH^-] = 1 \times 10^{-14}$$
$$[OH^-] = \frac{1 \times 10^{-14}}{2 \times 10^{-10}}$$
$$= 0.5 \times 10^{-4}$$
$$\therefore \text{NaOH} = 5.0 \times 10^{-5}\text{M}$$

We need 250 ml of 5×10^{-5}M NaOH

$$\text{litres} \times \text{M} = \text{number of moles}$$
$$0.25 \times 5 \times 10^{-5} = \text{number of moles}$$
$$1.25 \times 10^{-5} \text{ moles.}$$
$$\frac{\text{Weight in grams}}{\text{Molecular weight}} = \text{Number of moles}$$
$$\text{Weight in grams} = \text{Number of moles} \times \text{Molecular weight}$$
$$= (1.25 \times 10^{-5}) \times 40$$
$$= 50 \times 10^{-5} \text{ g.}$$

Problem 5.2. What are the mole fractions of solute and solvent in a 1.00 m equeous solution?

Solution. The molecular weight of water is 18.00. The number of moles of water in 1000 g H_2O, $= \dfrac{1{,}000 \text{ g}}{18.0 \text{ g}} = 55.5$ mol H_2O

A 1.00 m equeous solution contains

$$n_{solute} = 1.00 \text{ mol}$$
$$n_{H_2O} = 55.5 \text{ mol}$$
$$n_{total} = 56.5 \text{ mol}$$

∴ the mole fraction of solute, X_{solute}

$$=\frac{n_{solute}}{n_{total}}=\frac{1.00\text{ mol}}{56.5\text{ mol}}=0.018$$

mole fraction of solvent, X_{H_2O}

$$=\frac{n_{H_2O}}{n_{total}}=\frac{55.5\text{ mol}}{56.5\text{ mol}}=0.982$$

Problem 5.3. Calculate the vapour pressure over a solution containing 11.7 g benzene and 4.6 g methylbenzene at 50°C, if the vapour pressures of the pure components at this temperature are 3.6×10^4 Nm^{-2} and $1.12\times10^4\text{Nm}^{-2}$, respectively.

Solution. Number of moles of benzene present$=\frac{11.7}{78}=0.15$

Number of moles of methyl benzene present$=\frac{4.6}{92}$

$=0.05$

Hence,

Total number of moles$=0.20$

Molefraction of benzene $(x_A)=\frac{0.15}{0.20}=0.75$

Molefraction of methylbenzene $(x_B)=\frac{0.05}{0.20}=0.25$

Partial pressure of benzene, $P_A=x_AP^\circ_A$

$=0.75\times3.6\times10^4$

$=2.7\times10^4\text{Nm}^{-2}$

Similarly, partial pressure of methylbenzene

$=0.25\times1.12\times10^4$

$=0.28\times10^4\text{Nm}^{-2}$

∴ Total vapour pressure of the mixture$=2.98\times10^4\text{Nm}^{-2}$

Problem 5.4. Ten grams of the "antifreeze" ethylene glycol, $C_2H_6O_2$, is dissolved in 450 grams of water. Calculate the molality of the solution.

Solution. Moles of $C_2H_6O_2=\frac{\text{Weight}}{\text{MW}}=\frac{10.0\text{ g}}{62.0\text{ g/mole}}$

$=0.16$ mole

$$\text{Molality, } m=\frac{\text{Moles } C_2H_6O_2}{\text{kg water}}$$

$$m=\frac{0.16\text{ mole}}{0.450\text{ kg}}$$

$=0.36$ mole per kg.

Problem 5.5. Calcium hydroxide $Ca(OH)_2$, is to be reacted with phosphoric acid, H_3PO_4, to give calcium phosphate, $Ca_3(PO_4)_2$, and water. Two solutions are prepared by adding 5.0 grams of $Ca(OH)_2$ to water to give 500 ml of solution and by adding 10.0 gram of H_3PO_4 to water to give 750 ml solution. Calculate the normality of the $Ca(OH)_2$ and H_3PO_4 solutions.

Solution. One mole of $Ca(OH)_2$ accepts two moles of protons in the reaction. Therefore the equivalent weight of $Ca(OH)_2$ is half the formula weight i.e. $\frac{1}{2}\times 74.2=37.1$. One mole of H_3PO_4 donates three moles of H^+ in the reaction, so the equivalent weight $\frac{1}{3}\times 98.0=32.6$.

$$\text{Equivalents } Ca(OH)_2=\frac{\text{Weight of } Ca(OH)_2}{\text{Equivalent weight}}=\frac{5.0\text{ grams}}{37.1\text{ grams}}$$

$$=0.13\text{ equivalent}$$

$$\text{Equivalent } H_3PO_4=\frac{\text{Weight of } H_3PO_4}{\text{Equivalent weight}}=\frac{10.0}{32.3}$$

$$=0.30\text{ equivalent.}$$

From the definition of normality,

$$N[Ca(OH)_2]=\frac{0.13\text{ equivalent}}{0.500\text{ litre solution}}$$

$$=0.26\text{ equivalent per litre.}$$

$$N(H_3PO_4)=\frac{0.30\text{ equivalent}}{0.750\text{ litre}}$$

$$=0.40\text{ equivalent per litre.}$$

Problem 5.6. A solution to be used as a hand lotion is prepared by mixing 90.0 grams of water, 6.40 grams of methyl alcohol and 18.40 grams of glycerol. Calculate the mole fraction of glycerol.

Solution. The number of moles of each component is found from moles=weight/molecular weight

$$\text{Moles } H_2O=\frac{90.0}{18.0}=5.0$$

$$\text{Moles } CH_3OH=\frac{6.40}{32.00}=0.20$$

$$\text{Moles } C_3H_8O_2=\frac{18.40}{92.0}=0.20$$

Mole fraction of glycerol is

$$X=\frac{0.20}{5.0+0.20+0.20}=0.037.$$

Problem 5.7. The solubility of N_2 in water is 2.2×10^{-4} g in 100 grams of H_2O at 20°C when the pressure of nitrogen over the solution is 1.2 atm. Calculate the solubility at that temperature when the nitrogen pressure is 10 atm.

Solution. Nitrogen concentration $[N_2]=KP_{N_2}$

$$2.2\times10^{-4}\ g=K\ (1.2\ atm)$$

$$K=\frac{1.2\times10^{-4}}{1.2\ atm}=1.8\times10^{-4}\ g/atm$$

$$[N_2]=(1.8\times10^{-4}\ g/atm)\ (10\ atm)$$

$$=1.8\times10^{-3}\ g.$$

Problem 5.8. Calculate the mole fraction of water consisting of 9.0 g of water, 120 g of acetic acid, and 115 g of ethyl alcohol.

Solution. The molecular weights of water, acetic acid and ethyl alcohol are 18, 60 and 46 respectively. The mixture thus contains 0.50 mole of water, 2.0 mole of acetic acid and 2.5 mole of ethyl alcohol.

Total number of moles=5.0

$$\text{Mole fraction of } H_2O=\frac{0.50}{5.0}$$

$$=0.10.$$

Problem 5.9. The vapour pressure of pure benzene and toluene at 60° are 385 and 139 torr respectively. Calculate the partial pressures of benzene and toluene, the total vapour pressure of the solution, and the mole fraction of toluene in the vapour above the solution with 0.60 mole fraction toluene.

Solution. $P_{\text{benzene}}=(0.40)\ (385\ \text{Torr})=154.0\ \text{Torr}$

$$P_{\text{toluene}}=(0.60)\ (139\ \text{Torr})=83.4\ \text{Torr}$$

$$\text{Total}=237.4\ \text{Torr}$$

$$X_{\text{toluene vapour}}=\frac{83.4}{237.4}$$

$$=0.351.$$

Problem 5.10. Through their gill systems, fish breathes the dissolved air present in water. Though the concentration of air in water is not great, show that the air which a fish breathes is richer in oxygen percentagewise than ours. The partial pressure of oxygen in air is 0.20 atm and that of nitrogen is 0.80 atm at 20°C. The Henry's law constant for oxygen is 4.1×10^4 atm; for nitrogen it is 8.3×10^4 atm.

Solution. The solubility of O_2 and N_2 in water in terms of mole fraction, can be calculated as follows,

$$X_{O_2}=P_{O_2}/K_{O_2,H_2O}$$

$$X_{O_2}=\frac{0.20\text{ atm}}{4.1\times 10^4\text{ atm}}$$

$$X_{O_2}=4.9\times 10^{-6}$$

and

$$X_{N_2}=P_{N_2}/K_{N_2,H_2O}$$

$$=\frac{0.80\text{ atm}}{8.30\times 10^4\text{ atm}}$$

$$=9.6\times 10^{-6}.$$

Thus, the dissolved air a fish breathes is thus $\frac{1}{3}$ oxygen, which is greater than the $\frac{1}{5}$ oxygen present in the air we breathe.

Problem 5.11. What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.400 with a mole fraction of benzene of 0.600?

Solution. $P^{\circ}_{\text{benzene}}=119$ torr

$P^{\circ}_{\text{toluene}}=37.0$ torr

$P_{\text{benzene}}=(0.400)\ (1.19\text{ torr})=47.6$ torr

$P_{\text{toluene}}=(0.600)\ (37.0\text{ torr})=22.2$ torr

$P_{\text{total}}\ =47.6\text{ torr}+22.2\text{ torr}=69.8$ torr

The composition of the vapour is determined by applying Dalton's law of partial pressures

$$N_{\text{benzene vapour}}=\frac{P_{\text{benzene}}}{P_{\text{total}}}$$

$$=\frac{47.6\text{ torr}}{69.8\text{ torr}}$$

$$=0.682$$

$$N_{\text{toluene vapour}}=1.00-0.682$$

$$=0.318$$

$$=\frac{22.2}{69.8}\text{torr}$$

Similarly for the case of the solution in which the mole fraction of toluene is 0.400.

$$N_{\text{benzene vapour}}=\frac{71.5}{86.3}=0.829$$

$$N_{\text{toluene vapour}}=\frac{14.8}{86.3}=0.171$$

Problem 5.12. Nitro-benzene can be distilled with steam under a pressure of one atmosphere at a temperature of 99.2°C. Calculate the amount of steam necessary to distil 100 g of nitrobenzene. The vapour pressure of water at 99.2°C is 739 mm Hg.

Solution. Weight of water=?

Weight of nitro-benzene=100 g

Total pressure $P_{total}=760$ mm

P_A partial pressure of water at 99.2°C=739 mm

P_B partial pressure of nitro-benzene at 99.2°C=760—739

=21 mm

M_A molecular weight of water=18 g

M_B molecular weight of nitrobenzene=123 g

$$W_A=\frac{W_B P^\circ_A . M_A}{P^\circ_B . M_B}$$

$$=\frac{100\times 739\times 18}{21\times 123}$$

$$W_A=515 \text{ g.}$$

The weight of steam required will be 515 g.

Problem 5.13. The solubility at 20°C of potassium chlorate is 8 and of potassium chloride is 32 g/100 g H_2O. What crystals would deposit first if solutions, initially at 100°C and containing

(*a*) 0.1 mole potassium chloride, 0.1 mole potassium chlorate and 100 g water.

(*b*) 35 g potassium chloride, 0.06 mole potassium chlorate and 100 g water, were cooled to 20°C?

Solution. 1 mole of potassium chloride weighs 74.5 g and 1 mole potassium chlorate weighs 122.5 g. Therefore, solution (*a*) contains 7.45 g potassium chloride and 12.25 g potassium chlorate per 100 g water. It is thus quite clear that the solubility of potassium chlorate is exceeded when the solution is cooled to 20°C, while that of potassium chloride is not. Hence the deposit will consist of potassium chlorate.

Solution (*b*) contains 35 g potassium chloride and 122.5×0.06 or 7.35 g potassium chlorate per 100 g water. In this case the crystalline deposit will consist of potassium chloride, since its solubility has been exceeds on cooling.

Problem 5.14. A solution is prepared from 10.6 g of a non-volatile, non-dissociating solute and 90.0 g of water. The vapour pressure of the solution at 60°C is 0.1867 atm. Use Raoult's law to find the approximate molecular weight of the solute. The vapour pressure of water at 60°C is 0.1966 atm.

Solution. $P_{total}=X_{H_2O}P^\circ_{H_2O}$

$$0.1867 \text{ atm} = X_{H_2O}(0.1966 \text{ atm})$$
$$X_{H_2O} = 0.9496.$$

The mole fraction of the solute in the solution, therefore, is

$$X_{solute} = 1 - X_{H_2O}$$
$$= 1 - 0.9496$$
$$= 0.0504$$

Number of moles of water used in the preparation of the solution.

$$n_{H_2O} = 90.0 \text{ g } H_2O \left(\frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O}\right)$$
$$= 5.00 \text{ mol } H_2O$$

The mole fraction of solute is equal to the number of moles of solute present divided by the total number of moles.

$$X_{solute} = \frac{n_{solute}}{n_{H_2O} + n_{solute}}$$

$$0.0504 = \frac{n_{solute}}{5.00 + n_{solute}}$$

$$n_{solute} = 0.265 \text{ mol.}$$

$$\text{Molecular weight of the solute} = \left(\frac{10.6 \text{ g solute}}{0.265 \text{ mol solute}}\right) \times 1.00 \text{ mol solute}$$
$$= 40.0 \text{ g.}$$

Problem 5.15. Vapour pressure of a pure liquid is 100 torr at 25°C while its vapour pressure from 95 mole per cent solution at the same temperature is only 90 torr. What is the activity of the liquid in the solution? What is the activity coefficient for it?

Solution. In this case vapour pressures also represent the fugacities of the liquid in the pure and solution states, the activity can thus be calculated. Pure liquid state will be the standard state of the liquid.

$$\therefore \quad f = \frac{90 \text{ torr}}{760 \text{ torr/atm}} = \frac{90}{760} \text{ atm.}$$

$$f^\circ = \frac{100}{760} \text{ atm}$$

$$\therefore \quad a = \frac{f}{f^\circ} = \frac{90}{760} \times \frac{760}{100} = 0.9$$

$$a_1 = \gamma_1 X_1 \quad \text{where } X_1 = \frac{95}{100} = 0.95$$

$$\therefore \quad \gamma_1 = \frac{a_1}{X_1} = \frac{0.90}{0.95} = 0.95$$

Problem 5.16. Two liquids A and B form an ideal solution at

50°C. A liquid mixture containing one mole of A and two moles of B to the mixture shows a vapour pressure of 250 torr. When one more mole of A is added to the mixture its vapour pressure increases to 300 torr. Calculate the vapour pressures of the liquids *A* and *B* at 50°C.

Solution. $P_{mixture}=X_A P^\circ_A+X_B P^\circ_B$

For the first solution:

$$X_A=0.33, \quad X_B=0.66$$

For the second solution

$$X_A=0.50, \quad X_B=0.50$$

$$\therefore \quad 250=0.33P^\circ_A+0.66P^\circ_B$$

$$300=0.50P^\circ_A+0.50P^\circ_B$$

On multiplying first equation by 3 and second by 2, we get

$$P^\circ_A+2P^\circ_B=750$$

$$P^\circ_A+P^\circ_B=600$$

$$P^\circ_B=150, \quad P^\circ_A=450 \text{ torr.}$$

EXERCISES

5.1. A solution is prepared by dissolving 15.6 g benzene, C_6H_6, in 500 g of carbon tetrachloride, CCl_4. The volume of the solution is 450 ml. Calculate (*i*) molarity, (*ii*) molality, (*iii*) the boiling point of the solution.
[**Ans.** (*i*) 0.40 m, (*ii*) 0.44 m, (*iii*) 2.01°C.]

5.2. The label on a bottle of aqueous sulphuric acid, H_2SO_4, gives its concentration as 44.0 per cent by weight, and the density of the solution is listed as 1.31 g/ml. Convert the information to (*i*) molarity, (*ii*) molality, (*iii*) mole fraction.
[**Ans.** (*i*) 5.9 M, (*ii*) 8.0 m, (*iii*) 0.13.]

5.3. How many litres of 5M H_2SO_4 are required to make (*a*) 1500 ml of a 0.002 M H_2SO_4 solution, and (*b*) 1500 ml of 0.002 N H_2SO_4?
[**Ans.** (*a*) 0.6 ml, (*b*) 0.3 ml.]

5.4. Calculate the weight of solid NaOH required to prepare (*a*) 5 litres of a 2M solution, (*b*) 2 litres of a solution of pH 11.5, and (c) 500 ml of 62 per cent W/W solution. The density of 62 per cent NaOH solution is 1.15 g/ml.
[**Ans.** (*a*) 400 g NaOH, (*b*) 356 g.]

5.5. Henry's law constant for nitrogen at 20°C is 5.75×10^7. How many grams nitrogen would dissolve in 100 g of water at 20°C, if the pressure of nitrogen over the solution is 750 mm?
[**Ans.** 2.02×10^{-3} g.]

5.6. The vapour of pure ethylene dibromide, $C_2H_4Br_2$, at 85°C is 170 mm Hg. Calculate the partial vapour pressure of ethylene dibromide above an ideal solution at 85°C with a mole fraction of ethylene dibromide of 0.250.
[**Ans.** 42.5 mm Hg.]

5.7. Using the Henry's law constant, calculate the solubility of carbon dioxide in water at 25°C at a partial pressure of CO_2 over the solution of 760 torr.

Assume that a litre of solution contains practically 1000 grams of water. Henry's law constant for CO_2 is 1.25×10^6. [**Ans.** 3.38×10^{-2} M.]

5.8. If the vapour pressure of pure *A* is 234 mm Hg at 20°C, what would be the partial vapour pressure of *A* above an ideal solution at 20°C, if the mole fraction of *A* is equal to 0.250? [**Ans.** 58.5 mm Hg.]

5.9. The vapour pressure of pure propylene dibromide, $C_3H_6Br_2$, at 85°C is 130 mm Hg. Assuming ideal behaviour calculate the partial vapour pressure of $C_3H_6Br_2$ for the following solutions at 85°C.

(*a*) $X_{C_3H_6Br_2} = 0.250$

(*b*) $X_{C_3H_6Br_2} = 0.500$

c) $X_{C_3H_6Br_2} = 0.750$.

[**Ans.** (*a*) 32.5 mm Hg, (*b*) 65.0 mm Hg, (*c*) 97.5 mm Hg.]

5.10. Calculate the total vapour pressure of the following solution at 20°C.

$X_{C_6H_6} = 0.750$

$X_{CH_3C_6H_5} = 0.250$

Assume ideal behaviour. [**Ans.** 60.8 mm Hg.]

5.11. A solution consists of 2.80 moles of acetone, CH_3COCH_3, and 8.20 moles of chloroform, $CHCl_3$. Calculate the mole fraction of acetone.

[**Ans.** 0.254.]

5.12. A solution consists of 1.0 mole of ethyl bromide, CH_3CH_2Br, and 3.0 moles of propyl bromide, $CH_3CH_2CH_2$ Br. What is the mole fraction of ethyl bromide? [**Ans.** 0.250.].

5.13. A solution is made by mixing together 7.80 g of benzene, C_6H_6, and 46.0 g of toluene, C_7H_8. Calculate the mole fraction of benzene in the solution. Molecular weight of benzene is 78.0 and that of toluene 92.10.

[**Ans.** 0.167.]

5.14. Ethanol and methanol form nearly ideal solutions. The vapour pressure of ethanol is 44.5 torr, and that of methanol is 88.7 torr, at 20°. (*a*) Calculate the mole fraction of methanol and ethanol in a solution obtained by mixing 100 g of each. (*b*) Calculate the partial pressures and the total vapour pressure of the solution. (*c*) Calculate the mole fraction of methanol in the vapour.

[**Ans.** (*a*) $X_{C_2H_5OH} = 0.410$; $X_{CH_3OH} = 0.590$; (*b*) $p_{C_2H_5OH} = 18.2$,

$p_{CH_3OH} = 52.3$, $p_{Total} = 70.5$ torr; (*c*) 0.741.]

5.15. A mixture of benzene $p_{benzene} = 268$ mm and ethylene chloride $p_{C_2H_5Cl_2} = 236$ mm behaves ideally at 50°C What is the total vapour pressure of a liquid mixture containing equal weights of the two components? What is the molar composition of the vapour?

[**Ans.** $P_{total} = 254$ mm; mole fraction, benzene $= 0.591$,

$C_2H_4Cl_2 = 0.409$.]

5.16. The vapour pressure of pure substances *A* and *B* are 110.0 and 220.0 mm Hg respectively at 25°C. Calculate the mole fraction of each component in the vapour phase over an equimolar solution, if the solution is ideal.

[**Ans.** $A = \frac{1}{3}$ mole, $B = \frac{3}{2}$ mole.]

5.17. Ethyl acetate and ethyl propionate form nearly ideal solutions over the entire range of compositions. At 20°C vapour pressure of ethyl acetate is 72.8 mm Hg and of ethyl propionate is 27.7 mm Hg (*a*) Calculate the vapour pressure of liquid mixture containing 25 g of ethyl acetate and 50 g of ethyl propionate. (*b*) Calculate the mole fractions of each in the vapour phase.

[**Ans.** (*a*) 44.2 mm Hg; (*b*) $X_{\text{ethyl acetate}}=0.604$

$X_{\text{ethyl propionate}}=0.396$.]

5.18. Two pure liquids *A* and *B* have vapour pressures of 200 and 500 torr respectively at 300 K. Calculate the mole per cent of *A* and *B* in the liquid and vapour phases of a mixture *C* which has a vapour pressure of 350 torr.

[**Ans.** $X_A=0.286$, $X_B=0.714$.]

5.19. A solutions of liquids *A* and *B* containing 30 mole per cent of *B* is in equilibrium with the vapour containing 60 mole per cent of *B*. Calculate the ratio of the vapour pressures of more and less volatile of the liquids *A* and *B* in the pure state. [**Ans.** 3.5.]

5.20. The boiling point of the immiscible liquid system naphthalene-water is 98°C under a pressure of 733 mm. The vapour pressure of water at 98°C is 707 mm. Calculate the weight per cent of naphthalene in the distillate.

[**Ans.** 20.7 per cent.]

5.21. *A* and *B* form a constant boiling solution at a maximum temperature at $X_A=\frac{1}{3}$. When a mixture of 1 mole of *A* and one of *B* is fractionally distilled, how much pure *A* is obtained? The boiling point of pure *A* is 110°C, of pure *B* is 150°C. Does *A* come off the top of the column or collect in the pot?

[**Ans.** $\frac{1}{2}$ mole pure *A*, $1\frac{1}{2}$ mole azeotrope. The *A* comes off the top.]

5.22. A liquid mixture contains substances *A* which boils at 300 K and substance *B* which boils at 500 K. No azeotrope is formed between *A* and *B*. At 200 K, is the vapour richer or poorer in *B* than the liquid?

[**Ans.** poorer.]

5.23. At 100°C benzene has a vapour pressure of 1357 mm and toluene has a vapour pressure of 558 mm. Assuming that these substances form ideal binary solutions with one another, calculate the composition of the solution that will boil at 100°C and the vapour composition.

[**Ans.** $X_{\text{benzene, liq}}=0.253$, $X_{\text{benzene, vap}}=0.451$.]

5.24. A mixture of chlorobenzene and water is distilled at an external pressure of 740.2 mm. It is found to boil at a temperature of 90.3°C Calculate the composition of the distillate. Given the vapour pressure of pure water at 90.3°C is 530.1 mm.

[**Ans.** $C_6H_5Cl=40.14$ per cent by weight, $H_2O=59.86$ per cent by weight.]

5.25. When aniline is steam distilled, the distillate is found to contain 27.1 per cent by weight of aniline. What is the ratio of the vapour pressures of aniline and water at the temperature of distillation? [**Ans.** 1 : 13.92.]

5.26. A mixture of nitrobenzene and water distils at 98.2° at a pressure of 731.9 mm and the weight ratio of nitrobenzene and water in the distillate is 0.188. The vapour pressures of water and nitrobenzene at this temperature are 712.4 mm and 19.5 mm respectively. Calculate the molecular weight of the nitrobenzene. [**Ans.** 124 g mole^{-1}.]

5.27. The saturated vapour pressure of benzene and toluene are both given by the equation

$$\log_{10}(P/N)=\frac{-0.05223A}{T}+B$$

where T is the thermodynamic temperature and A and B have the following values:

	A	B
Benzene	32295 K	9.7795
Toluene	39128 K	10.4549

Assuming that mixtures of benzene and toluene form ideal solutions. Calculate the molar percentage of benzene in (*a*) mixture which boils at 97°C under an external pressure of 1 atm and (*b*) the initial concentrate formed on distilling this mixture.

(**Hint.** 1 atm$=1.013\times10^5$ Nm^{-2}. Using the above equation calculate p°_B and p°_A for benzene and toluene respectively. The mole fraction of benzene in the vapour (in the initial condensate) formed on distilling the above condensate is equal to partial pressure of benzene divided by the total pressure i.e., 1.013×10^5 Nm^{-2}.)

[**Ans.** (*a*) 0.210, (*b*) 0.346.]

5.28. The saturated vapour pressures at 50°C of CCl_4 and $SiCl_4$ are 0.424×10^5 Nm^{-2} and 0.800×10^5 Nm^{-2} respectively. Assuming ideal behaviour, calculate (*a*) the mole fraction of $SiCl_4$ in a mixture boiling at 50°C under an external pressure of 0.533×10^5 Nm^{-2} and (*b*) the mole fraction of $SiCl_4$ in the inital condensate formed on distilling this mixture.

[**Ans.** (*a*) mole fraction of $SiCl_4$ in liquid$=0.29$, (*b*) mole fraction of $SiCl_4$ in initial condensate$=0.435$.]

5.29. The vapour pressure of the system diethylaniline-water is 1.013×10^5 Nm^{-2} at 99.4°C. The vapour pressure of water at this temperature is 0.992×10^5 Nm^{-2}. How many grams of steam are necessary to distil over 100 g of diethyl aniline? [**Ans.** 571 g.]

5.30. The vapour pressures of bromobenzene and water at 95°C are 125 mm and 635 mm respectively. A mixture of two liquids on being steam distilled at 95°C gives a distillate consisting of 100 g of bromobenzene and 58 g of water. Calculate the molecular weight of bromobenzene. [**Ans.** 157.5.]

6

COLLIGATIVE PROPERTIES

INTRODUCTION

At any temperature, there exists an equilibrium, when the escaping tendency of molecules in the liquid and vapour, is the same. On raising the temperature, the escaping tendency of liquid increases. More liquid will evaporate until the vapour pressure rises to the point at which the escaping tendency of vapour molecules back into the liquid is equal to the tendency of the liquid molecules to evaporate. This equilibrium pressure of vapour above a liquid is known as the equilibrium vapour pressure of the substance. In the pure liquid water, every molecule that approaches the surface has a certain chance of escaping into the vapour phase, depending on its kinetic energy. If a non-volatile solute, say, sugar is added, so that one molecule in ten is sugar and not water, then only 90 per cent of the molecules that formerly were potential escapes have a possibility of getting out of the liquid. The average escaping tendency of water molecules from a given amount of solution is reduced, but the rate of condensation is unaffected since no sugar molecules are present in the vapour. Thus condensation goes ahead of vaporization so more vapour condense. Thus the equilibrium vapour pressure of the sugar solution will be 90 per cent of that of the original solution. This relative lowering of vapour pressure was studied by Raoult. If a non-volatile solute A is added to a pure solvent B and let X_A and X_B be the respective mole fractions of solvent and solute respectively. If P° is the vapour pressure of the pure solvent and P is the vapour pressure of the solution.

$$P = P^\circ X_A \qquad \ldots (1)$$

Since X_A is a positive quantity and is smaller than unity, therefore P is always less then P°. Hence whenever a non-volatile solute is added to a solvent, the effect is the lowering of vapour pressure of the solvent

$$\begin{aligned}\triangle P &= P^\circ - P \\ &= P^\circ - P^\circ X_A\end{aligned}$$

$$\triangle P = P^\circ(1-X_A)$$

$$X_A+X_B = 1, \qquad 1 - X_A = X_B$$

$$\therefore \quad \frac{\triangle P}{P^\circ} = X_B \qquad \ldots (2)$$

Hence the relative lowering of vapour pressure is equal to the mole fraction of the solute. The mole fraction of the solute, X_B

$$X_B = \frac{n_B}{n_A + n_B} \qquad \ldots (3)$$

where n_B is the number of moles of solute and n_A is the number of moles of solvent

$$n_B = \frac{W_B}{M_B}\,;\; n_A = \frac{W_A}{M_A} \qquad \ldots (4)$$

$$\therefore \quad \frac{\triangle P}{P^\circ} = \frac{W_B/M_B}{W_A/M_A + W_B/M_B} \qquad \ldots (5)$$

Boiling Point Elevation

Since the boiling point is defined as that temperature at which the vapour pressure equals the atmospheric pressure. Anything that lowers the vapour pressure of the solution will raise its boiling point. The boiling elevation in dilute solution, is found to be directly proportional to the solute concentration

$$\triangle T_b = K_b m. \qquad \ldots (6)$$

$\triangle T_b$ is the boiling point elevation. K_b is the boiling point elevation constant, and m is the molality

$$\triangle T_b = K_b . \frac{W_B}{M_B} . \frac{1000}{W_A} \qquad \ldots (7)$$

$$\text{or } M_B = K_b . \frac{1000}{\triangle T_b} . \frac{W_B}{W_A} \qquad \ldots (8)$$

K_b is defined as,

$$K_b = \frac{RT_o^2}{1000\, l_v} \qquad \ldots (9)$$

where l_v is the heat of vaporization per gram of solvent, T_o is the boiling point of the pure solvent.

Freezing Point Depression

This is the temperature at which the precipitation of the solid solvent begins. At this temperature, solid solvent and solution are in equilibrium and consequently they must have the same vapour pressures. The freezing point depression $\triangle T_f$ is given by

$$\triangle T_f = K_f m. \qquad \ldots (10)$$

K_f is known as the molal depression constant. It is also given by,

$$K_f = \frac{RT_o^2}{1000\, l_f} \qquad \ldots (11)$$

l_f is the latent heat of fusion per gram of solvent

$$\triangle T_f = K_f . \frac{W_B}{M_B} . \frac{1000}{W_A} \qquad \ldots (12)$$

or $$M_B = K_f . \frac{W}{\triangle T_f} . \frac{1000}{W_A} \qquad \ldots (13)$$

Osmosis and Osmotic Pressure

Abbe Nollet observed that when a solution of alcohol and water was separated by an animal bladder and placed in pure water, the water passed through the bladder into the alcohol solution, but the alcohol could not pass into the water. This passage of solvent through a membrane into a solution is known as osmosis. This passage of water into the alcohol solution results in an increase of pressure in the solution. This increase in pressure, which is addition to the vapour pressure of the solution is known as the osmotic pressure and is denoted by π. If V is the volume of solution in litres containing one mole of solute and n_2 is the number of moles of solute in V litres of solution, we get the relation.

$$\pi V = n_2 RT. \qquad \ldots (14)$$

where R is the gas constant and T is the temperature of the solution. Equation (14) can also be written as,

$$\pi = CRT \qquad \ldots (15)$$

where $C = n_2/V$

Osmotic pressure is also a colligative property as it depends only on the number of moles of solute and not on its chemical nature, at a given temperature.

The van't Hoff's Factor

When a solute dissolves in a solvent if there occurs, either partial association or dissociation, in such cases the use of the colligative property equations leads to erroneous results. This is because the colligative properties depend upon the number of solute particles present. On dissociation the solute particles may simply produce smaller molecules or they may form ions. However, in either case the number of solute particles is increased, and this multiplication of particles will result in an increase in the colligative properties, than would otherwise have been the case. If association occurs, the number of solute particles is observed and the colligative properties will consequently be smaller than would have been expected if no association occurs.

The van't Hoff factor *i* may be defined as the ratio of the observed value of the colligative property for a solution to the value calculated from the molality of the solution, i.e.,

$$i = \frac{\triangle T_b}{(\triangle T_b)_o} = \frac{\triangle T_f}{(\triangle T_f)_o} = \frac{\pi}{(\pi)_o} \qquad \ldots (16)$$

where $(\triangle T_b)_o$, $(\triangle T_f)_o$ and $(\pi)_o$ are the boiling point elevation, freezing point depression and osmotic pressure respectively of the non-electrolyte. The van't Hoff factor measures the increase in the colligative properties for electrolytes. Hence, this must mean that electrolytes contribute more particles to the solution than do the non-electrolytes for the same molalities.

Problem 6.1. Calculate the quantity of nitrogen (in g) dissolved by 100 cm^3 of blood plasma when this is aerated at 311 K and 102.7 kPa. (Absorption coefficient of N_2 in plasma at 311 K = 0.012; air contains 78 per cent N_2 by volume.)

Solution. The absorption coefficient of N_2 in plasma at 311 K = 0.012 implies that 0.012 cm^3 (at STP) of N_2 dissolves in 1 cm^3 of plasma at 311 K and standard atmospheric pressure (i.e., 101.325 kPa), therefore, 100 cm^3 of plasma at 311 K and 101.325 kPa will dissolve 1.2 cm^3 (at STP) of N_2.

Partial pressure N_2 in air at 102.7 kPa = 78/100 × 102.7 kPa. According to Henry's law, $S = K_\alpha P$

or $$\frac{S_1}{S_2} = \frac{P_1}{P_2}$$

Solution of pure N_2 at 101.325 kPa

$$S_1 = 1.2 \text{ cm}^3\ N_2/100 \text{ cm}^3 \text{ plasma}$$
$$P_1 = 101.325 \text{ kPa}$$

Solution of N_2 from air at 102.7 kPa

$$S_2 = ?\ \text{cm}^3/100 \text{ cm}^3 \text{ plasma}$$
$$P_2 = \frac{78 \times 102.7}{100} \text{ kPa}$$
$$\frac{102}{S_2} = \frac{101.325 \times 100}{1.027 \times 78}$$

$$S_2 = \frac{1.2 \times 1.027 \times 78}{101.325 \times 100}$$

$$= 0.949 \text{ cm}^3 \text{ of } N_2/100 \text{ cm}^3 \text{ plasma.}$$

Since 24.414 cm³ (at STP) of N_2 has a mass of 28.0 g

$$\therefore 0.949 \text{ cm}^3 \text{ (at STP) of } N_2 \text{ has a mass} = \frac{0.949 \times 28}{24.414 \times 10^3} \text{ g}$$

$$= 1.186 \times 10^{-8} \text{ g.}$$

Hence 100 cm³ of blood plasma will dissolve 1.186 mg N_2 when aerated under the above conditions.

Problem 6.2. At 310 K the vapour pressure of glycerol is negligible compared with that of water. If the vapour pressure at 310 K above 56 per cent glycerol solution in water was 4772 Pa, calculate the activity of water in this solution. (Vapour pressure of water at 310 K is 6275 Pa).

Solution. The vapour pressure above the glycerol solution at 310 K is virtually entirely due to water vapour. Vapour pressure of water above the solution, $p = 4772$ Pa, vapour pressure of pure water at the same temperature $p^\circ = 6275$ Pa,

Activity of water in the solution

$$= \frac{p}{p^\circ} = \frac{4772}{6275} = 0.76.$$

Problem 6.3. A solution contains 1.0 mole of ethyl bromide, CH_3CH_2Br, and 3.00 moles of propyl bromide, $CH_3CH_2CH_2Br$. What is the mole fraction of ethyl bromide?

Solution. $$X_{\text{ethyl bromide}} = \frac{n_{\text{ethyl bromide}}}{n_{\text{propyl bromide}} + n_{\text{ethyl bromide}}}$$

$$= \frac{1.00 \text{ mole}}{3.00 \text{ mole} + 1.00 \text{ mole}}$$

$$= \frac{1.00}{4.00}$$

$$= 0.250.$$

Problem 6.4. The vapour pressure of pure ethylene dibromide, $C_2H_4Br_2$ at 85°C is 170 mm Hg. Calculate the partial vapour pressure of ethylene bromide above an ideal solution at 85°C with a mole fraction of ethylene dibromide of 0.250.

Solution. $$P_{C_2H_4Br_2} = P^\circ_{C_2H_4Br_2} \times X_{C_2H_4Br_2}$$

$$= (170 \text{ mm Hg}) \times (0.250)$$

$$= 42.5 \text{ mm Hg.}$$

Problem 6.5. Calculate the mole fraction of benzene in the vapour phase that is in equilibrium with the following solution at 20°C, assuming ideal behaviour,

$$X_{\text{benzene}} = 0.500$$
$$X^{e}_{\text{toluene}} = 0.500$$
$$P_{\text{total}} = 47.5 \text{ mm Hg at } 20°\text{C}.$$

Solution.
$$X^{V}_{C_6H_6} = \frac{X^{P}_{C_6H_6}\, P^{\circ}{}_{C_6H_6}}{P_{\text{total}}}$$
$$\approx \frac{(0.500)(74.2 \text{ mm})}{(47.5 \text{ mm})}$$
$$= 0.781$$

Problem 6.6. Caculate the osmotic pressure at 25°C of solution containing one gram of glucose ($C_6H_{12}O_6$) and one gram of sucrose ($C_{12}H_{22}O_{11}$) in 1000 g of water. If it were not known that the solute was a mixture of glucose and sucrose, what would be the molecular weight of the solute, corresponding to calculated molecular weight.

Solution. $\pi = \frac{n_t}{V} \cdot RT$

where n_t is the total number of moles, i.e.,

$$n_t = n_{\text{glucose}} + n_{\text{sucrose}}$$

$$n_{\text{glucose}} = \frac{1}{180} \text{ (molecular weight of } C_6H_{12}O_6 = 180)$$

$$n_{\text{sucrose}} = \frac{1}{342} \text{ (molecular weight of } C_{12}H_{22}O_{11} = 342)$$

$$n_t = \frac{1}{180} + \frac{1}{342}$$
$$= 0.00848 \text{ mole}$$
$$V = 1 \text{ litre.}$$
$$R = 0.082\ l \text{ atm K}^{-1} \text{ mole}^{-1}$$
$$T = 298 \text{ K}$$
$$\pi = \frac{0.00848 \text{ mole}}{1\ l} \times 0.082\ l \text{ atm K}^{-1} \text{ mole}^{-1}$$
$$= 0.2072 \text{ atm.}$$

$$\pi = \frac{n}{V} . RT$$

$$\pi = \frac{\frac{W}{M}}{V} \times RT.$$

W = weight of solute = 2 g

M = molecular weight of the solute

$\pi = 0.2072$ atm

$R = 0.082\ l$ atm deg^{-1} mole^{-1}

$T = 298$ K

$$0.2072 = \frac{2}{M} \times 0.082 \times 298$$

$$M = \frac{2 \times 0.082 \times 298}{0.2072}$$

$$M = 235.87.$$

Problem 6.7. A solution containing 4.0 g of polyvinyl chloride polymer in 1 litre of dioxane was found to have an osmotic pressure of 6.4×10^{-4} atm at 27°C. Calculate the approximate molecular weight of the polymer.

Solution. Let M be the molecular weight of the polymer

$$n = \frac{4.0}{M}$$

$$\pi = \frac{n}{V} RT.$$

$V = 1$ litre

$R = 0.082$

$T = 273 + 27 = 300$ K

$\pi = 6.4 \times 10^{-4}$

$$M = \frac{4.0\ RT}{\pi . V}$$

$$= \frac{4.0 \times 0.082 \times 300 \times 7}{6.4 \times 10^{-4} \times 22}$$

$$M = 1.538 \times 10^5$$

Problem 6.8. What is the concentration of a solution of canesugar which is isotonic with solution containing 6 g of urea per litre? Given that the molecular weight of cane-sugar is 342 and that of urea is 60.

Solution. $\pi_{\text{sugar}} = C_{\text{sugar}}\ RT$

Let W be the weight of sugar isotonic with urea.

$$\pi_{\text{urea}} = C_{\text{urea.}}\ RT$$

Since the solutions are isotonic

$$\pi_{\text{sugar}} = \pi_{\text{urea}}$$

$$C_{\text{sugar.}}\ RT = C_{\text{urea.}}\ RT.$$

$$\frac{W}{342} = \frac{6}{60}$$

$$W=\frac{6}{60}\times 342$$

$$=34.2 \text{ g.}$$

Problem 6.9. An aqueous solution contains 75 g of glucose in 250 ml of the solution at 300 K. What is the osmotic pressure of the solution?

Solution. The molecular weight of glucose is $C_6H_{12}O_6$

$$=6(12.0)+12(1.00)+6(16.00)$$

$$=180$$

$$n=\frac{75.0 \text{ g}}{180 \text{ g}} \text{ mole}$$

$$\pi=0.417 \text{ mole}$$

$$\pi=\left(\frac{n}{V}\right)RT$$

$$\pi=\frac{0.417}{0.250}\times 0.082\times 300$$

$$\pi=41 \text{ atm.}$$

Problem 6.10. An aqueous solution containing 5 g dm^{-3} a soluble polysaccharide has an osmotic pressure of 3.24 kPa at 278 K. Assuming ideal behaviour, calculate the molecular weight of the polysaccharide. ($R=8.314$ JK^{-1} mol^{-1})

Solution. Molecular weight, M of a polysaccharide

$$=\frac{CRT}{\pi}$$

where,

$\pi=3.24$ kPa
$C=5\times 10^3$ gm^{-3}
$R=8.314$ JK^{-1} mol^{-1}
$T=278$ K

$$\text{Molecular weight, } M=\frac{(5.0\times 10^3)\times 8.314\times 278}{3.24\times 10^3}$$

$$=3567 \text{ g mol}^{-1}.$$

Problem 6.11. An aqueous solution containing 5 g dm^{-3} of a soluble polysaccharide has an osmotic pressure of 3.24 kPa at 278 K. Calculate the molecular weight of the polysaccharide, assuming the solution to behave ideally.

Solution. $$\pi=\frac{C}{M}RT$$

$$M=\frac{CRT}{\pi}$$

where,

$$\begin{aligned}\pi&=3.24\text{ kPa}\\&=3.24\times10^{3}\text{ Nm}^{-2}\\C&=5\times10^{3}\text{ gm}^{-3}\\R&=8.314\text{ JK}^{-1}\text{ mole}^{-1}\\&=8.314\text{ Nm K}^{-1}\text{ mole}^{-1}\\T&=278\text{ K}\\M&=?\\M&=\frac{(5\times10^{3})\times8.314\times278}{3.24\times10^{3}}\\&=3567\text{ g mole}^{-1}.\end{aligned}$$

Problem 6.12. A 1.2 per cent solution of NaCl is isotonic with 7.2 per cent solution of glucose. Calculate the van't Hoff's factor i of NaCl solution. Molecular weight of glucose is 180 and that Na=23 and Cl=35.5.

Solution. $$\pi_{\text{glucose}}=\frac{7.2}{180}\times10.RT$$

$$\pi_{\text{NaCl}}=\frac{1.2\times10}{M}.\,RT$$

Since the two solutions are isotonic we have,

$$\pi_{\text{glucose}}=\pi\text{NaCl}$$

$$\frac{7.2\times10}{180}=\frac{1.2\times10}{M_{\text{obsd.}}}$$

$$M_{\text{obsd.}}=\frac{1.2\times10\times180}{7.2\times10}$$

$$=30.$$

Calculate molecular weight of NaCl=23+35.5

$$M_{\text{calc.}}=58.5$$

$$\text{van't Hoff's factor } i=\frac{M_{\text{obsd.}}}{M_{\text{cacl.}}}$$

$$=\frac{30}{58.5}$$

$$=0.51.$$

Problem 6.13. The vapour pressure of water at 20°C is 17.54 mm of mercury and the vapour pressure of a solution of 108.24 g of a compound in 1000 g of water at the same temperature is 17.354 mm of mercury. Calculate the molecular weight of the substance.

Solution. Let M_2 be the molecular weight of the substance

$$P^\circ = 17.54 \text{ mm}, \quad P = 17.354 \text{ mm}$$

$$\frac{P^\circ - P}{P^\circ} = X_2$$

X_2 is the mole fraction of the solute, i.e.,

$$X_2 = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1}$$

n_1 is the number of moles of solvent and n_2 is the number of moles of solute

$$X_2 = \frac{108.24}{M} \Big/ \frac{1000}{18}$$

$$\frac{17.54 - 17.354}{17.54} = \frac{108.24 \times 18}{M \times 1000}$$

$$M = \frac{108.24 \times 18 \times 17.54}{0.186 \times 1000} = 183.73 \text{ g.}$$

Problem 6.14. A solution contains 7.31 g urea in 50 g of water. When air was bubbled through this solution and then successively through water and concentrated sulphuric acid, the bulb containing pure water lost 0.087 g while a gain in weight of 2.036 g was noted for the sulphuric acid bulb. What is the weight of one mole of urea?

Solution. Loss in weight $\propto P_A$

Loss in weight of water bulb $\propto P^\circ_A - P_A \propto 0.087$

Gain in weight of sulphuric acid bulb $\propto P^\circ_A \propto 2.36$

Hence

$$P^\circ_A - P_A = \frac{0.087}{2.036} = x_B = 0.043$$

If M is the weight of one mole of urea, then

$$\text{Number of moles of water in solution} = \frac{50}{18} = 2.78$$

$$\therefore \quad x_B = \frac{7.31/M}{2.78 + \frac{7.31}{M}} = 0.043$$

$$M = 58.9.$$

Problem 6.15. A current of dry air is passed through a solution of 26.66 g of a substance in 200 g of water and then through water alone. The loss of weight of solution is 1.949 g and that of water 0.087 g. Calculate the molecular weight of dissolved substance.

Solution. $$\frac{p^\circ - p}{p^\circ} = X_2$$

$$= \frac{W_2}{M_2} \Big/ \frac{W_1}{M_1}$$

$$= \frac{W_2 M_1}{W_1 M_2}$$

$$W_2 = 26\ 66 \text{ g}$$

$$W_1 = 200$$

$$M_1 = 18.00$$

$$p \propto 1.949$$

$$(p^\circ - p) \propto 0.087$$

$$p^\circ \propto (1.949 + 0.087)$$

$$\frac{0.087}{2.036} = \frac{26.66 \times 18}{200 \times M_2}$$

$$M_2 = \frac{26.66 \times 18 \times 2.036}{200 \times 0.087}$$

$$M_2 = 56.15.$$

Problem 6.16. A solution containing 3.795 g sulphur in 100 g carbon disulphide boils at 46.66°C. The boiling point of pure carbon disulphide is 46.30 and $\triangle H_{vap} = 6400$ cal/mole. Calculate the molecular formula of sulphur in carbon disulphide.

Solution. $\triangle T_b = K_b\ m.$

where m is the molality of the solution, K_b is known as molal elevation constant and $\triangle T_b$ is the elevation of boiling point.

Also, $$K_b = \frac{R\ T_0^2 .\ M_1}{1000 .\ \triangle H_v}$$

where T_0 is the boiling point of pure solvent in K. M is the molecular weight of the solvent

$$K_b = \frac{1.98 \times 319.3 \times 319.3 \times 76}{1000 \times 6400} = 2.397$$

$$\triangle T_b = K_b \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$(46.66 - 46.30) = 2.397 \times \frac{3.795}{M_2} \times \frac{1000}{100}$$

$$M_2 = \frac{2.397 \times 3.795 \times 1000}{100 \times 0.36}$$

$$M_2 = 252.7.$$

The molecular formula of sulphur would be

$$\text{Number of sulphur atoms} = \frac{252.7}{32.00} \approx 8$$

Hence the molecular formula of sulphur in carbon disulphide will be S_8.

Problem 6.17. A solution of 0.450 g of urea in 22.50 g of water gave a boiling point elevation of 00.170°C. Calculate the molal elevation constant of water. The molecular weight of urea is 60.0.

Solution.

$$\triangle T_b = K_b\, m$$

$$K_b = \frac{\triangle T_b}{m}$$

$$m = \frac{0.450 \times 1000}{60 \times 22.5}$$

$$\triangle T_b = 0.170°\text{C}$$

$$K_b = \frac{0.170 \times 60 \times 22.5}{0.450 \times 1000}$$

$$= 0.51°\text{C mole}^{-1}.$$

Problem 6.18. A 0.1 M solution of KNO_3 has an osmotic pressure of 4.5 atm at 27°C. Calculate the apparent degree of dissociation of the salt in this solution.

Solution.

$$\pi_{obs} = 4.5 \text{ atm}$$

$$C = 0.1 \text{ mole/litre}$$

Let the degree of dissociation is denoted by α and the number of dissociation fragments obtained from each undissociated molecule of the solute is x and C moles per litre is the total concentration of the solute in terms of undissociated molecules,

Moles per litre before dissociation $= C$

Moles per litre after dissociation $= C(1-\alpha)+Cx\alpha$

$= C\{1+(x-1)\alpha\}$ moles/litre

A colligative property $i = \dfrac{C\{1+(x-1)\alpha\}}{C}$

$$\therefore \quad \alpha = \frac{i-1}{x-1}$$

$$x = 2 \text{ ions/molecule}$$

$$R = 0.082 \text{ litre-atm/mole/deg}$$

$$T = 273+27 = 300 \text{ K}$$

$$\therefore \quad 4.5 = 0.1\{1+(2-1)\alpha\}0.082 \times 300$$

$$\alpha = \frac{4.5}{0.1 \times 0.082 \times 300} - 1$$

$$\alpha = \frac{4.5}{2.6} - 1$$

$$\alpha = 1.83 - 1$$

$$\alpha = 0.83 \quad \text{or} \quad 83 \text{ per cent.}$$

Problem 6.19. Propanone boils at 56.38°C, and a solution of 1.41 g of an organic solid X in 20 g of propanone boils at 56.88°C. If K_b for propanone is 16.7, calculate the weight of one mole of X.

Solution. If 20 g of propanone contain 1.41 g of X, then 100 g of propanone would contain

$$\frac{1.41 \times 100}{20} = 7.05 \text{ of } X$$

Since

$$\triangle T_b = \left(\frac{W}{M}\right) K_b$$

$$56.88 - 56.38 = \frac{7.05}{M} \times 16.7$$

$$M = \frac{7.05 \times 16.7}{0.50}$$

$$M = 235.$$

Problem 6.20. 250 g of water contain 0.1 mole of a non-volatile solute. Calculate the quantity of ice deposited when the solution is cooled to —3.72°C. K_f for water (100 g) is 18.6.

Solution. When the freezing point of the solution reaches —3.72°C, let x g of water remain in the liquid state. Then at —3.72°C, x g of water dissolve 0.1 mole solute and 100 g of water would dissolve

$$\frac{0.1 \times 100}{x} \text{ mole solute } \left(= \frac{W}{M}\right)$$

$$\triangle T = 3.72 = \frac{0.1 \times 100}{x} \times 18.6$$

$$x = \frac{0.1 \times 100 \times 18.6}{3.72} = 50 \text{ g.}$$

Since 250 g of water were initially present, the weight of ice deposited will be 200 g.

Problem 6.21. A 0.100 molal aqueous solution of a partially dissociated substance AB, freezes at —0.208°C. Calculate the per cent dissociation. K_f for water is 1.86 K.

Solution. If no dissociation takes place in 0.100 molal solution, the freezing point depression would be

$$\triangle T = K_f m$$

$$\triangle T=(1.86\ \text{deg/molal})(0.100\ \text{molal})$$
$$\triangle T=0.186\ \text{deg.}$$

Let x be the total concentration of particles in solution, then

$$\triangle T=(1.86)(x)=0.208$$
$$\therefore \quad x=\frac{0.208}{1.86}=0.112$$

If AB dissociates as follows:

$$\begin{array}{ccc} AB & \rightleftharpoons & A^+ + B^- \\ (0.100-y) & y & y \end{array}$$

The total concentration of particles is

$$(0.100-y)+y+y=0.112$$
$$y=0.012$$

This is the concentration of A^+ and B^- and the molality of AB molecules dissociated.

$$\text{Per cent dissociation}=\frac{0.012}{0.100}=12\ \text{per cent.}$$

Problem 6.22. How many grams of glucose do you need to consume (*a*) to climb a flight stairs rising through 3 m, (*b*) to climb a mountain of altitude 3000 m? The heat of combustion of glucose is —2808 kJ mol^{-1}. Assume that 25 per cent of the enthalpy can be converted to useful work and the weight of your body to be 63 kg. (Molecular weight of glucose is 180.2 g mol^{-1})

Solution. (*a*) Since $W=mgh$

where $m=63$ kg $g=9.8$ ms^{-2} h$=3$ m

$$W=(63\ \text{kg})\times(9.8\ \text{ms}^{-2})\times(3\ \text{m})$$
$$W=1852\ \text{J}$$
$$W=1.852\ \text{kJ}$$

$$\text{The heat of combustion for 1 g of glucose}=\frac{2808\ \text{kJ}}{180.2\ \text{g mol}^{-1}}$$
$$=15.58\ \text{kJ g}^{-1}.$$

$$\text{At 25 per cent efficiency}\triangle H_c=\frac{15.58}{4}=3.90\ \text{kJ mol}^{-1}$$

Thus we see that for 1.85 kJ the required consumption is,

$$(1.85\ \text{kJ})/(3.90\ \text{kJ g}^{-1})=0.47\ \text{g}$$

(*b*) $W=(63\ \text{kg})(9.8\ \text{ms}^{-1})\times(3000\ \text{m})=18.52\ \text{kJ}$;

$\therefore$ the required consumption of glucose is $0.47\times1000=0.47$ kg.

Problem 6.23. The freezing point of pure benzene is 5.40°C and that of a solution containing 2.0 g of solute per 100 g benzene is 4.40°C. Calulate the molecular weight of the solute. Molal depression constant for benzene is 5°C.

Solution. $$\Delta T_f = K_f \,.\, m$$

ΔT_f is the depression in freezing point K_f is molal depression constant, m is the molality of the solution

$$\Delta T_f = K_f . \frac{W_2 \times 1000}{M_2 . \, W_1}$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f . \, W_1}$$

$$M_2 = \frac{5.00 \times 2.00 \times 1000}{1.00 \times 100}$$

$$M_2 = 100.$$

Problem 6.24. Calculate the osmotic pressure at 303 K of an aqueous solution of sucrose which at standard atmospheric pressure has a freezing point 0.093 K lower than water. (Molal depression constant of water=1.86 K.)

Solution. The molecular weight M_B of the solute is given by the expression

$$M_B = K_f \times \frac{1000 \, W_B}{\Delta T_f \times W_A}$$

where $\dfrac{1000 \, W_B}{W_A} = C' =$ g solute/1000 g solvent.

In dilute aqueous solutions C' is approximately equal to 10^{-3} C where C is the concentration in g^{-3},

$$M_B = \frac{K_f C'}{\Delta T_f}$$

$$M_B = \frac{K_f \, (10^{-3} C)}{\Delta T_f}$$

According to the van't Hoff osmotic equation, $M_B = CRT/\pi$

$$\frac{K_f \, (10^{-3}) C}{\Delta T_f} = \frac{CRT}{\pi}$$

$$\pi = \frac{10^3 \times \Delta T_f \times RT}{K_f}$$

$$\Delta T_f = 0.093 \text{ K}$$

$$R = 8.314 \text{ Nm K}^{-1}\text{mole}^{-1}$$

$$T = 303\ \text{K}$$

$$K_f = 1.86\ \text{K}$$

$$\pi = \frac{10^3 \times 0.093 \times 8.314 \times 303}{1.86}\ \text{Nm}^{-2}$$

$$\pi = 1.26 \times 10^5\ \text{Nm}^{-2}$$

$$\pi = 126\ \text{kPa}.$$

Problem 6.25. If the depression of freezing point of 0.01 mole dm^{-3} aqueous solution of propionic acid at standard atmospheric pressure is -0.0193 K. Calculate an approximate value for the ionization constant of propionic acid in this solution at approximately 273 K.

Solution. The van't Hoff's factor for this solution of propionic acid is given by

$$i = \frac{\triangle T_f}{(\triangle T_f)_o}$$

where $\triangle T_f$ = observed depression of freezing point.

$(\triangle T_f)_o$ = Calculated depression of freezing point of the non-electrolyte.

$$\therefore \qquad i = \frac{\triangle T_f}{(\triangle T_f)_o} = \frac{0.0193}{0.0186} = 1.037$$

The degree or ionization of propionic acid $\alpha = \dfrac{i-1}{n-1}$

where $i = 1.037$

$$n = 2$$

$$\alpha = \frac{1.037-1}{2-1} = 0.037$$

Ionization constant, $K = \dfrac{\alpha^2 C}{1-\alpha}$

$$K = \frac{(0.037)^2 \times 0.01}{1-0.037}$$

$$K = 1.42 \times 10^{-5}.$$

Problem 6.26. A 0.100 m acetic acid solution is found to have an osmotic pressure of 2.479 atm at 25°C. What is the per cent dissociation of acetic acid at this temperature and concentration?

Solution. $\pi = imRT$

or $$i = \frac{\pi}{mRT}$$

$$i = \frac{2.479}{(0.100)\ (0.0821)\ (298.2)}$$

$$i = 1.013.$$

If acetic acid were completely dissociated, i would equal 2. If acetic acid were undissociated, i would equal 1. Since 1.013 is 1.3 per cent of the way between 1 and 2, the acid is 1.3 per cent undissociated.

Problem 6.27. A satellite is orbiting where the acceleration of gravity has decreased to 5 m/s². What is weight in orbit of an astronaut whose weight at sea level is 900 newtons?

Solution. The mass of the astronaut is, $m = \frac{Fg}{g'} = \frac{900\text{N} \times 1\ \text{kgm/Ns}^2}{9.8067}$

$$m = 91.77\ \text{kg}.$$

In orbit the force exerted by the pull of gravity on the 91.77 kg mass is

$$F = \frac{mg'}{g} = \frac{91.77 \times 5\ \text{m/s}^2}{1\ \text{kg m/Ns}^2}$$

$$F = 458.9\ \text{N}.$$

Problem 6.28. Phenol partially associates into double molecules when dissolved in water. In a solution of 1.880 g of phenol in 100.0 g of water freezes at —0.210°C, calculate the degree of association of phenol molecules at the freezing point of the solution. K_f for water is 1.86°C.

Solution. Phenol associates according to the reaction,

$$\begin{array}{ccc} 2C_6H_5OH & \rightleftharpoons & (C_6H_5OH)_2 \\ 1 - \alpha & & \alpha/2 \end{array}$$

Total solute moles in solution per mole of phenol

$$= 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

Moles of phenol actually added to the solution $= \frac{1.880}{94}$

Final moles of solute in 100 g of water $= \frac{1.880}{94}\left(1 - \frac{\alpha}{2}\right)$

$$\Delta T_f = 1000 \times 1.86 \times \frac{1.88\left(1 - \frac{\alpha}{2}\right)}{94 \times 100}$$

$$0.210 = \frac{18.6 \times 1.81}{94} \times \left(1 - \frac{\alpha}{2}\right)$$

$$\frac{\alpha}{2} = 0.435$$

$$\alpha = 0.87 \text{ or } 87 \text{ per cent.}$$

EXERCISES

6.1. What of the following observations illustrate colligative properties?

(*a*) The blue colour of 1.0 $CuSO_4$ solution is more intense than that of 0.24 M $CuSO_4$.

(*b*) Pure benzene boils 20°C lower than pure water at 1.00 atm.

(*c*) Saturated salt water boils at higher temperature than pure water at 760 torr.

(*d*) The taste of 1.0 M NaCl is quite different from that of 1.0 M glucose.

(*e*) The osmotic pressure of 1.0 M NaCl is nearly twice that of 1.0 M glucose at the same temperature. [**Ans.** (*a*), (*c*) and (*e*).]

6.2. Indicate observations illustrating colligating properties.

(*a*) Pure benzoic acid begins to freeze at 122°C, while pure water begins to freeze at 0°C.

(*b*) A saturated aqueous solution of benzoic acid begins to freeze below 0°C.

(*c*) A saturated aqueous benzoic acid tastes sour, while a saturated sodium benzoate solution tastes somewhat salty.

(*d*) 0.010 M sodium benzoate solution has an osmotic pressure nearly twice that of 0.010 M benzoic acid solution. [Ans. (*b*) and (*d*).]

6.3. Fill in the blanks:

(*a*) Two moles of sugar are added to 500 g of water solvent. The molality of the resulting solution is————.

(*b*) A solution contains 3 moles of solute and 12 moles of solvent. What is the mole fraction of the solvent?

(*c*) In a solution of benzene and toluene if toluene accounts for a mole fraction of 0.6, what is the benzene mole fraction?

(*d*) A sugar water solution of 7.0 m would increase the boiling point by ————.

(*e*) The freezing point change for a 2.5 m solution of sugar would be ————.

(*f*) The molality of a sugar water solution that freezes at —3.50°C is ————.

[**Ans.** (*a*) 4.0 m, (*b*) 0.8, (*c*) 0.4, (*d*) 3.57°C, (*e*) —4.65°C, (*f*) 1.88 m.]

6.4. A solution containing 58 g of acetone (CH_3COCH_3), 69 g of ethyl alcohol (C_2H_5OH) and 63 g of H_2O, what is mole fraction of water in this mixture? [**Ans.** 0.58.]

6.5. Calculate the vapour pressure of an aqueous 1.00 m glucose solution at 100°C. [Ans. 746 mm Hg.]

6.6. What is the vapour pressure of an aqueous solution of 30.0 g of urea, $(NH_2)_2CO$, dissolved in 200 g of water at 25°C? The vapour pressure of pure H_2O at 25°C is 23.8 torr. [Ans. 22.8 torr.]

6.7. Calculate the vapour pressure lowering of a solution containing 100 g of sucrose ($C_{12}H_{25}O_{11}$) in 500 g of water at 25°C is 23.76 mm of Hg. [Ans. 0.24 mm Hg.]

6.8. The vapour pressure of water at 20°C is 17.54 mm of mercury and the vapour pressure of a solution of 108.24 g of a compound in 1000 g of water at the same temperature is 17.354 mm of mercury. Calculate the molecular weight of the compound. [**Ans.** 181.7.]

6.9. At a certain temperature the vapour pressure of water is 92 mm of Hg. The vapour pressure of water is reduced to 87 mm on dissolving 18.2 g of a solute in 100 g of water. Calculate the molecular weight of the solute. **[Ans. 56.87.]**

6.10. At 0°C the vapour pressure of pure water is 4.85 mm of Hg and that of solution containing 8.8 g of solute per 100 g of water is 4.85 mm of Hg. Calculate the molecular weight of the substance. **[Ans. 345.46.]**

6.11. A solution of 11.346 g of turpentine in 100 g of ether (mol. wt. 74) has a vapour pressure of 360.1 mm. Calculate the molecular weight of turpentine. Vapour pressure of pure ether at the same temperature is 383 mm Hg. **[Ans. 140.5.]**

6.12. 18.2 g of urea dissolved in 100 g of water at 50°C causes lowering of vapour pressure equal to 5 mm Hg. The vapour pressure of water at 50°C is 92 mm Hg. Calculate the molecular weight of urea. **[Ans. 60.28.]**

6.13. A solution containing 9.81 g of a substance *X* in 100 g of water has a vapour pressure of 755.2 mm at 100°C. What is the molecular weight of the solute? **[Ans. 277.7.]**

6.14. In Walker-Ostwald experiment, air was drawn through a solution of 57.0 g of solute in 150.0 g of water and then through water. The loss in weight of water was 0.0827 g and the weight of water absorbed in sulphuric acid tube was 3.3176 g. Calculate the molecular weight of the solute. **[Ans. 280.7.]**

6.15. A current of dry air is passed through a solution of 26.66 g of a substance in 200 g of water and then through water alone. The loss of weight of solution is 1.949 g and that of water is 0.087 g. Calculate the molecular weight of the solute. **[Ans. 56.16.]**

6.16. A solution was prepared by dissolving 10 g of a substance in 200 g of benzene. When a stream of air was passed through the solution lost its weight by 2.66 g. When the same volume of air was passed through pure benzene at the same temperature, the loss in weight was 2.80 g. What is the molecular weight of the dissolved substance? **[Ans. 47.15.]**

6.17. The vapour pressure of carbon tetrachloride at 19°C is 85.513 mm Hg. The vapour pressure above a solution containing 0.5455 g of a substance in 25 g of carbon tetrachloride at the same temperature is 83.923 mm Hg. Calculate the molecular weight of this substance and determine its empirical formula, if the results of elementary analysis are as follows: C=94.30 per cent, H=5.66 per cent. **[Ans. 177.1.]**

6.18. Calculate the osmotic pressure of a solution of cane-sugar containing 100 g per litre at 30°C. **[Ans. 7.26 atm.]**

6.19. 2.00 g of sugar having molecular weight of 342 is dissolved in 50 ml of solution at 25°C. What will be the osmotic pressure? **[Ans. 2.86 atm.]**

6.20. Calculate the osmotic pressure in millimetres of mercury at 15°C of 1.4 per cent solution of naphthalene, $C_{10}H_8$, in benzene. **[Ans. 1960 mm.]**

6.21. A solution containing 0.312 per cent of a substance gives an osmotic pressure of 1.27 atmospheres at 25°C. Calculate the molecular weight of the substance. **[Ans. 60.02.]**

6.22. A solution containing 20 g of a substance in a litre of water has an osmotic pressure of 3 atmospheres at 27°C. Calculate the molecular weight of the substance. **[Ans. 160.]**

6.23. A solution of an unknown sugar gave an osmotic pressure of 2.39 atm at 27°C. The concentration of the given solution was 18 g per litre. Calculate the molecular weight of sugar. [Ans. 181.8.]

6.24. 7.2 g of a substance dissolved in 100 g of water gave rise to an osmotic pressure of 9.65 atm at 22°C. Calculate the molecular weight of the substance. [Ans. 180.0.]

6.25. The vapour pressure of water under 10 atm pressure is increased from 30 to 31 mm Hg at 25°C. How much NaCl would be added to 55.5 moles of water at 25°C so that the vapour pressure of the solution under 10 atm pressure would be 30 mm Hg? Calculate the osmotic pressure of this solution. Assume NaCl to form an ideal solution. [Ans. 0.88 mole.]

6.26. Solution of NaCl of concentration *m* has an osmotic pressure of 2.0 atm at 25°C. Calculate $\triangle G_{298}$ for the process H_2O (solution, 25°C) = H_2O (Pure, 25°C). [Ans. 36 c.c. atm.]

6.27. A membrane permeable only to water, separates a 0.01 M solution of sucrose from 0.001 M. On which solution must pressure be applied to bring the system into equilibrium? Calculate this osmotic pressure assuming ideal solutions at 25°C.

[Ans. A differential pressure of 0.225 atm would have to be applied to more concentrated solution.]

6.28. The osmotic pressure of blood is 7 atm at 30°C. What is the molarity of the solution, if the *i* factor for sodium choride is 1.9? [Ans. 0.148 m.]

6.29. What minimum pressure must be applied to a 0.20 M aqueous sodium chloride solution enclosed by a semi-permeable membrane at 27°C in order to initiate the reverse osmosis?

[Ans. Reverse osmosis would require 9.8 atm.]

6.30. A protein isolated from blood serum sample was found on careful analysis to contain 0.285 per cent iron. A colloidal dispersion of 685 mg of the protein in sufficient water to form 10.00 ml of solution was found to have an osmotic pressure of 0.21 atm at 4°C. What is the apparent molecular weight of protein to three significant figures? [Ans. 7.8×10^4.]

6.31. A colloidal dispersion of 12.3 g of a polystyrene plastic in 100 ml of toluene was found to have an osmotic pressure of 0.032 atm at 20°C. What is the apparent formula weight of polystyrene? [Ans. ~92.000.]

6.32. The osmotic pressure of a solution of 1.80 g of serum albumin in 100 g of water at 25°C is 76.7 mm of water. Calculate (*a*) the molecular weight of the solute and (*b*) the freezing point of the solution.

[Ans. (*a*) 59,000, (*b*) −0.006°C.]

6.33. If a solution containing 6.06 g of triphenyl methane, $(C_6H_5)_3CH$, in 1000 g of benzene is cooled to 0.221°C below the freezing point of pure benzene: (*a*) how much solvent will crystallize out, and (*b*) what will be the molality of the residual solution? [Ans. (*a*) 434 g, (*b*) 0.0438.]

6.34. Ten grams of glucose, dissolved in 400 g of ethanol elevated the boiling point of the latter by 0.1428°C, 2 g of an organic substance dissolved in 100 g of ethanol, elevated the boiling point 0.1250°C. What is the molecular weight of the unknown substance in this solution? [Ans. 164.6.]

6.35. The heat of vaporization of ethanol is 38,580 J. mole^{-1} and its boiling point is 351.7 K. Determine the boiling point elevation constant for ethanol.

[Ans. 26.7 per kg.]

6.36. A solution containing 0.3 g of camphor ($C_{10}H_{16}O$) in 25.2 g of chloroform boils at 61.3°C. Boiling point of chloroform is 60°C. Calculate ΔH and k_b of chloroform. **[Ans.** 8747 cal-mole^{-1}, 3.83°C mole^{-1}.]

6.37. A solution containing 0.7269 g of camphor (mol. wt.=152) in 38.08 g of acetone (of boiling point 56.30), boiled at 56.55°C. What is the molal elevation of boiling point and latent heat of vaporization of acetone. **[Ans.** K_b=1.99. l_u=108.2 cal. g^{-1}.]

6.38. A solution of 3.795 g sulphur in 100 g carbon disulphide (boiling point =46.3°C, $\Delta\ H_{vap}$=6400 cal mole^{-1}), boils at 46.66°C. What is the molecular formula of sulphur molecule in the CS_2 solution? **[Ans.** S_8.]

6.39. The boiling point of pure acetone is 56.4°C. A solution of 0.70 g of a compound in 10 g of acetone boiled at 56.9°C. What is the molecular weight of the compound? K_b for acetone is 1.67°C for 1000 g. **[Ans.** 236.1.]

6.40. The boiling point of chloroform was raised by 0.323°C when 1.0286 g of a substance was dissolved in 70 g of it. Calculate the molecular weight of the substance. K_b for chloroform is 3.9. **[Ans.** 177 5.]

6.41. Calculate the initial boiling points of the following solutions:
(*a*) 1.5 m glucose in ethanol.
(*b*) 1.5 m KNO_3 in water.
(*c*) 1.5 m K_2SO_4 in water. **[Ans.** 80.3°C, 101.6°C, 102.3°C.]

6.42. A solution containing 15 g of an unknown substance in 100 g of water has a boiling point of 100.255°C. What is the molecular weight of the unknown? **[Ans.** 300.]

6.43. Calculate the K_b for diethyl ether, $C_4H_{10}O$, given the following data. Boiling point of pure diethyl ether is 34.6°C. A solution of 6.80 g of benzoic acid, C_6H_5COOH, in 20.0 g of diethyl ether boils at 40.6°C. **[Ans.** 2.2°.]

6.44. The molal elevation constant K_b for CCl_4 is 5.02 deg/mole. The boiling point of pure CCl_4 is 76.8°C. Calculate the boiling point of a 1.00 molal solution of naphthalene $C_{10}H_8$ in CCl_4. **[Ans.** 102.1°C.]

6.45. 2.441 g of benzoic acid of 250 g of benzene lowers its melting point by 0.2048°C. What is the molecular formula of benzoic acid in this solvent? K_f of benzene is 5.12. **[Ans.** $(C_6H_5COOH)_2$.]

6.46. A solution containing 6.00 g of an unknown non-dissociating solute in 100 g of benzene is found to freeze at 276.28 K. With the same apparatus pure benzene is found to freeze at 278.66 K. What is the molecular weight of the solute? **[Ans** 28.0.]

6.47. The heat of fusion of cyclohexane is 2670 J. mole^{-1}, its freezing point is 279.7 K. Determine the freezing point depression constant for cyclohexane. **[Ans.** 20.5.]

6.48. A 21.6 mg sample of an organic compound was ground with 462 mg of camphor to form an intimate homogeneous mixture. A sample of the mixture was found to melt over the range 169.2–171.4°C. What is the apparent molecular formula weight of the compound? **[Ans.** 220.]

6.49. Estimate the initial freezing point of a saturated aqueous solution of sodium chloride, assuming saturation at 0°C. (Solubility of NaCl at 0°C is 35.7 g per 100 ml, K_b for water is—1.86). **[Ans.** 22.7°C.]

6.50. The latent heat of fusion of benzene is 30.25, 0.0802 g of a substance when dissolved in 13.03 g of benzene lowers the freezing point by 0.490°C. If pure benzene freezes at 5.4°C, calculate the molecular weight of the substance. [Ans. 64 36.]

6.51. Calculate the freezing point of a solution made by dissolving 42.0 g of mannoheptose, $C_7H_{14}O_7$ in 100 g of water. K_f for water is 1.86°C. [Ans. —3.72°C.]

6.52. Calculate the value of K_f for urethane given the following data. Freezing point of pure urethane is 49.7°C. A solution made by dissolving 10.0 g of a non-volatile organic solute, Z, in 30.0 g of urethane freezes at 36.5°C. Molecular weight of Z is 130. [Ans. 5.16°C.]

6.53. A solution made by dissolving 45.0 g of arabinose in 500 g of water freezes at —1.13°C. Calculate the molecular weight of arabinose. [Ans. 148 g/mole.]

6.54. A solution made by dissolving 90.0 g of glucose in 1000 g of water freezes at —0.93°C. Calculate the molality of this solution. [Ans. 0.50.]

6.55. Assume 100 per cent dissociation of solutes, what would be the freezing point depression for an aqueous solution that is 0.1 m in NaCl and 0.1 m in $CaCl_2$? $K_f = 1.86\ K_m^{-1}$ for water. [Ans. 0.5, 0.93°C.]

6.56. A newly synthesized organic compound was analysed for carbon and hydrogen and was found to contain 63.2 per cent by weight, 8.8 per cent hydrogen and the remainder oxygen. A solution of 0.0702 g of the compound in 0.804 g of camphor is found to freeze 15.3°C lower than the freezing of pure camphor. What are the molecular weight and formula of new compound? [Ans. $C_{12}H_{20}O_4$.]

6.57. A solution of 2.58 g phenol in 100 g bromoform freezes at a temperature 2.374°C lower than does pure bromoform. What is the apparent molecular weight of phenol at this concentration? [Ans. 157.]

7

SOLID STATE

INTRODUCTION

A crystalline solid is characterised by three criteria:

(*i*) A definite melting point.

(*ii*) A definite heat of fusion.

(*iii*) A definite crystal lattice.

The regular geometric pattern of the units making up a crystalline solid is called a crystal lattice. A lattice is a regular, three-dimensional arrangement of equivalent points in space.

There are seven crystal systems to describe the possible shapes of unit cells. All crystals are classified in terms of simple or complex unit cells derived from one of these types.

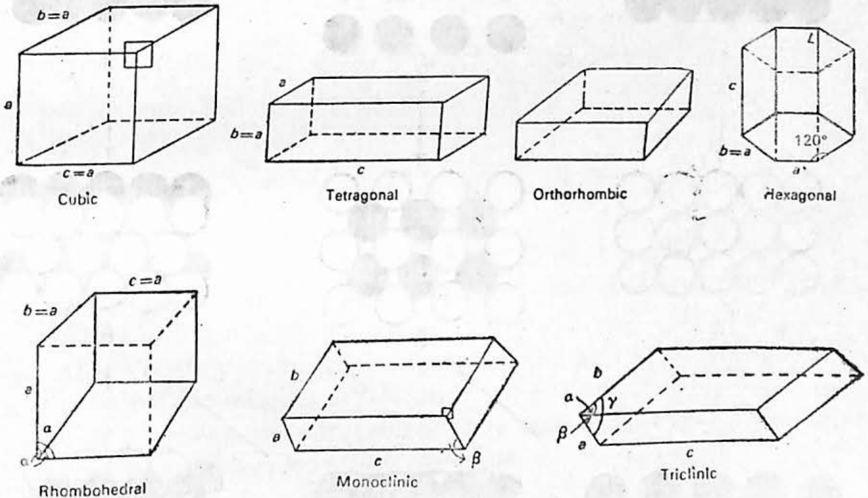


Fig. 7.1

The Seven Crystal Systems

X-ray diffraction is the method applied to determine the structure of solids. The actual arrangement of atoms, molecules or ions can be described in terms of space lattices, ordered arrays of particles diffract X-rays in a regular manner. In doing so the X-rays appear as though they have been reflected from the surface of the layers. In some cases the X-ray beam is reinforced and is detected at a specific angle of deflection where the intensity of the beam is at a maximum. Bragg found that reinforcement is dependent upon the wavelength of the X-rays, λ, the distance between the layers d, and the angle of incidence, θ, as

$$n\lambda = 2d \sin \theta$$

$$d = \frac{n\lambda}{2 \sin \theta}$$

As θ increases, $\sin \theta$ increases and *vice versa*. If a given set of planes of the crystals with a spacing equal to d is considered, it is seen that a scattered beam will be detected when $\sin \theta = \frac{\lambda}{2d}, \frac{2\lambda}{2d}, \frac{3\lambda}{2d}$ and so forth.

Packing of Atoms and Spherical Molecules

There are several ways in which a number of spheres of equal size

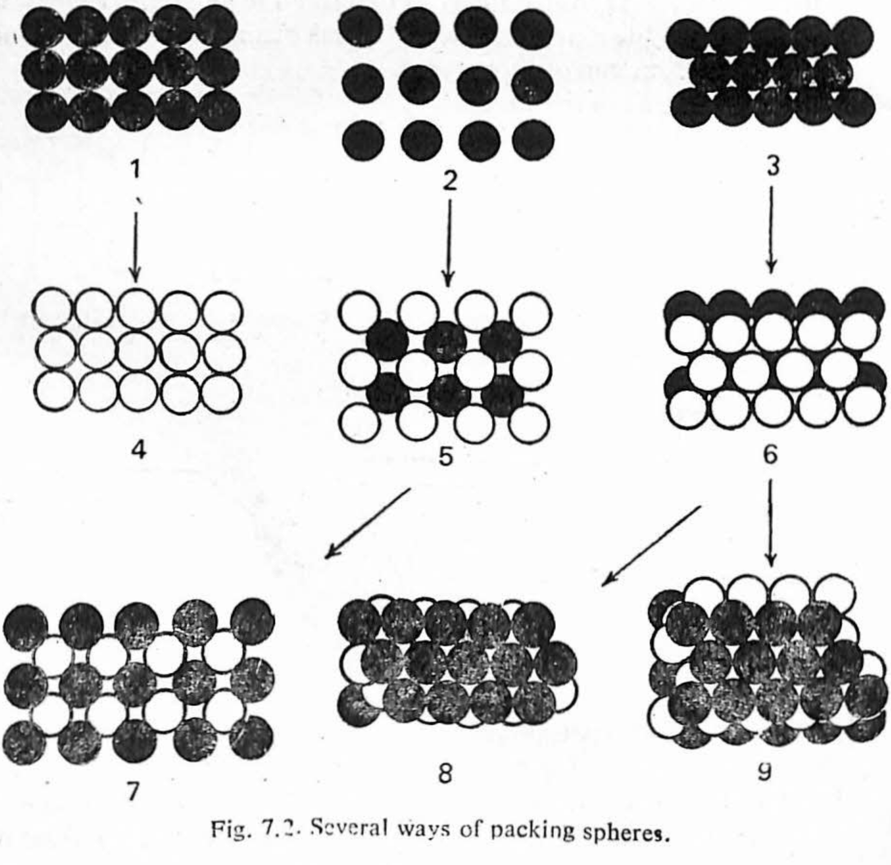


Fig. 7.2. Several ways of packing spheres.

can be packed in layers. Fig. 7.2 shows several ways of packing spheres.

The number of closest neighbours of a given sphere is called its co-ordination number. In both hexagonal closed packed (hcp) and cubic closed packed (ccp) lattices each sphere has 12 neighbouring spheres which it touches directly, 6 in the same plane, 3 in the plane, above and 3 in the plane below. Hence both closest packed structures have atoms characterised by coordination numbers of 12. The body centred cubic arrangement is less compact, the characteristic coordination number is 8. Many substances whose atoms or molecules are essentially spherical or whose molecules rotate freely in the lattice producing pseudospherical symmetry, crystallize is one or more of these lattice types.

Radius Ratio

The dimensions of the octahedral and tetrahedral sites in closest packed structures are determined by the sizes of the atoms occupying lattice points. Figure 7.3 shows the cross section of an octahedral site. Let r_1 be the radius of the spheres at the lattice points and r_2 is the radius of the largest possible smaller sphere occupying the octahedral site. The radius ratio, $\frac{r_2}{r_1}$ may be determined using Pythogorean theorem

$$2(r_1+r_2)^2 = (2r_1)^2$$

$$r_1+r_2 = \sqrt{2}.\, r_1$$

$$\therefore \quad \frac{r_2}{r_1} = 0.414.$$

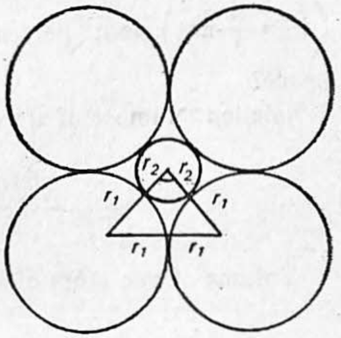


Fig. 7.3

(*i*) When the radius ratio is greater than 0.732 a coordination number of 8 is usually observed.

(*ii*) When the radius ratio is greater than 0.414 but less than 0.732, a coordination number of 6 is usually observed.

(*iii*) When the radius ratio is greater than 0.225 but less than 0.414 a coordination number of 4 is observed.

Lattice Energy

It is defined as the energy change observed when the constituents of a crystal are brought from infinitely far apart of their equilibrium positions in the crystal. A more complete expression for the lattice energy is given on next page.

$$U_o = \frac{Z_1 Z_2 N A e^2}{r_o}\left(1 - \frac{1}{n'}\right)$$

where U_o is the lattice energy, A is Madelung constant, N is Avogadro's number, n' is a constant called the Born exponent which can be obtained experimentally, Z_1 and Z_2 are the magnitudes of charges on the cation and anion respectively, r_o is the equilibrium distance.

The lattice energy of a crystal can be determined using Born-Haber cycle. This is because the steps may be shown graphically as a cyclic process.

Any one of the following constants for a crystal may be calculated provided the type of crystal lattice and all other constants are known.

(*i*) dimensions of the unit cell
(*ii*) density
(*iii*) atomic weight
(*iv*) Avogadro's number

Problem 7.1. The density of solid argon is 1.65 g per ml at—233°C. If the argon atom is assumed to be a sphere of radius 1.54×10^{-8} cm $\left(V = \frac{4}{3}\pi r^3\right)$, what percentage of solid argon is apparently empty space?

Solution. Number of atoms of argon in 1.65 g

$$= \frac{1.65}{40.0} \times 6.02 \times 10^{23}$$

$$= 2.48 \times 10^{22} \text{ atoms}$$

Volume of one atom of argon $= \frac{4}{3}\pi(1.54 \times 10^{-8})^3$

$= 1.53 \times 10^{-23}$ cm^3

Volume of 1.65 g of atoms $= (1.53 \times 10^{-23})(2.48 \times 10^{22} \text{ atoms})$

$= 0.379$ cm^3

Volume of 1.65 g of solid $= 1.00$ cm^3

per cent empty space $= (1.00 - 0.379) \times 100$

$= 62.1$ per cent.

Problem 7.2. Vanadium metal has a body centred cubic structure and the length of the unit cell is 3.04Å. (*i*) Calculate the volume of the unit cell in cubic centimetres (*ii*) If vanadium has a density of 5.96 g/cm^3, calculate the mass of one unit cell. (*iii*) How many vanadium atoms are in each unit cell of the element?

Solution. (*i*) Volume of vanadium $= (3.04\text{Å})^3 = 28.1\text{Å}^3$/unit cell

Since $1\text{Å} = 10^{-8}$ cm

Thus

$$\text{Volume}=\frac{28.1 \text{Å}^3 \times 10^{-24} \text{ cm}^3}{1 \text{ unit cell } \text{Å}}$$

$$=2.81 \times 10^{-23} \text{ cm}^3$$

(*ii*) Mass of one unit cell $=\frac{5.96 \text{ g } \times 2.81 \times 10^{-23} \text{ cm}^3}{\text{cm}^3 \text{ unit cell}}$

$$=1.67 \times 10^{-22} \text{ g/unit cell}$$

(*iii*) Number of vanadium atoms per unit cell 1/8 (8 atoms at corners)=1 atom

Number of vanadium atoms per unit cell$=\frac{1 \text{ atoms}}{2 \text{ atoms}}=\frac{1}{2}$

Problem 7.3. Determine the number of formula units of NaCl in the cell. NaCl is face centred cubic.

Solution. In the face centred cubic cell, there are at the eight corners $8 \times \frac{1}{8}=\text{Cl}^-$ ion

at the six faces $6 \times \frac{1}{2}=3 \text{ Cl}^-$ ions

along the 12 edges $12 \times \frac{1}{4}=3 \text{ Na}^+$ ions

at the cube centre $=1 \text{ Na}^+$ ion

Total 4 $\text{Cl}^-$and 4 Na^+ions.

Hence the unit cell contains four NaCl units.

Problem 7.4. Calculate the lattice energy of cesium iodide which crystallizes with the cesium chloride structure and has an interionic distance of 3.95 Å. The Born exponent for CsI is 12.

Solution. Madelung constant for CsI=1.76

Lattice energy, $U_o=-\frac{Z_1 Z_2 N A e^2}{r_o}\left(1-\frac{1}{n'}\right)$

$$U_o=\frac{-1.0 \times 1.0 \times 6.02 \times 10^{23} \times 1.76 \times (4.8 \times 10^{-10})^2}{3.95 \times 10^{-8}} \times \left(1-\frac{1}{12}\right)$$

$$U_o=-5.65 \times 10^{12} \text{ ergs mole}^{-1}$$

or $$U_o=-135.0 \text{ k. cal. mole}^{-1}.$$

Problem 7.5. The diffraction of crystal of barium with X-radiation of wavelength 2.29 Å gives a first order reflection at 27° 8′. What is the distance between the diffracted planes?

Solution. Bragg's equation is

$$n\lambda=2d \sin \theta$$

$$n=1,\ \lambda=2.29 \text{ Å},\ d=?,\ \theta=27°8'.$$

On substitution, $1\times 2.29\ \text{Å}=2d \sin 27°8'$

$$1\times 2.29=2d\,(0.456)$$

$$d=2.51\ \text{Å}.$$

Problem. 7.6. Nickel crystallizes in a face centred cubic crystal; the edge of the unit cell is 3.52Å. The atomic weight of nickel is 58.7, and its density is 8.94 g/cm³. Calculate Avogadro's number.

Solution. There are four nickel atoms in each unit cell. Let N be Avogadro's number, the weight of one atom is $(58.7/N)$ g. The weight of unit cell is 4 $(58.7/N)$ g. The value of one unit cell is $(3.52\times 10^{-8})^3$ cm³. The density of nickel is

$$\frac{4\,(58.7)/N}{(3.52\times 10^{-8})^3}=8.94\text{ g cm}^{-3}$$

$$\therefore \qquad N=6.02\times 10^{23}.$$

Problem 7.7. Calculate the atomic volume of an element whose atoms have a radius 1.414 Å when the atoms are in cubic closest packed structure. What is the length of an edge of the unit cell?

Solution. Diagonal of cube face $=4\times$ radius of atom length of the cell edge $=\frac{1}{\sqrt{2}}\times$ diagonal of cube face

$$=\frac{1}{\sqrt{2}}\times 4 \text{ radius of atom}$$

$$=\frac{1}{\sqrt{2}}\times 4\times 1.414\ \text{Å}$$

$$=4.0\ \text{Å}.$$

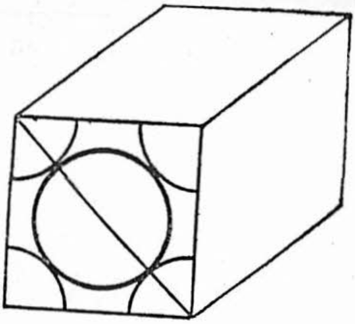


Fig. 7.4. Cubic closest packed (face centred) structure.

There are four atoms per unit cell in a face centred cubic atomic volume. Atomic volume

$$=\frac{(4.0\ \text{Å})^3}{1\text{ unit cell}}\times\frac{1\text{ unit cell}}{4\text{ atoms}}\times\frac{6.02\times 10^{23}\text{ atoms}}{1\text{ mole}}\times\left(\frac{1\times 10^{-8}\text{ cm}}{1\ \text{Å}}\right)^3$$

$$=9.6\text{ cm}^3/\text{mole}.$$

Problem 7.8. Compute the limiting radius ratio, r_+/r_-, for (*a*) a square planar crystal structure in which B^-ions are at the corners of the square and A^+ions at the centre, and (*b*) an equilateral triangular crystal structure with B^-at the apices and A^+at the centre.

Solution. (*a*) Length of unit cell edge $=2r_-$

Length of diagonal

$$=2r_+ + 2r_-$$

$$=\sqrt{2}\times \text{length of unit cell edge.}$$

$$2r_+ + 2r_- = 2\sqrt{2}r_-$$

$$2r_+ = \sqrt{2}r_- - r_-$$

$$= r_-(\sqrt{2}-1)$$

$$= r_-(1.414-1)$$

$$= 0.414r_-$$

$$\frac{r_+}{r_-} = 0.414.$$

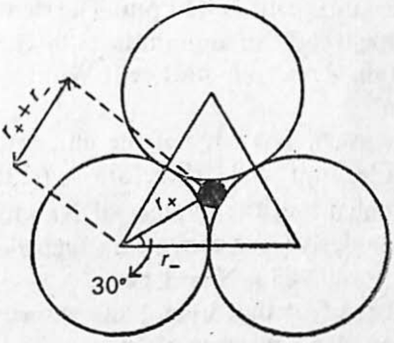


Fig. 7.5

(*b*) Sum of angles in a triangle $=180°$

Each angle in equilateral triangle $=60°$

The line shown in the diagram bisects the 60° angle.

$$\frac{r_-}{r_+ + r_-} = \text{Cos } 30°$$

$$=0.866$$

$$r_- = 0.866\ r_+ + 0.866\ r_-$$

$$0.866\ r_+ = 0.134\ r_-$$

$$\frac{r_+}{r_-} = \frac{0.134}{0.866} = 0.0155.$$

Problem 7.9. Potassium crystallises with a body centred cubic lattice and has a density of 0.856 g cm^{-3}. Calculate the length of the side of the unit cell *a* and the distance between (200), (110) and (222) planes.

Solution $0.856 \text{ cm}^{-3} = \dfrac{(2)\ (39.102 \text{ g mole}^{-1})}{(6.02205\times 10^{23} \text{ mole}^{-1})a^3}$

$$a = 5.333\times 10^{-8} \text{ cm} = 5.333 \text{ Å}$$

$$d_{hkl} = \frac{5.333}{\sqrt{h^2+k^2+l^2}}$$

For (200) planes, $d_{200} = \dfrac{5.333}{\sqrt{4}} = 2.667$ Å

For (110) planes, $d_{110} = \dfrac{5.33}{\sqrt{2}} = 3.771$ Å

For (222) planes, $d_{222} = \dfrac{5.33}{\sqrt{12}} = 1.540$ Å.

Problem 7.10. Sodium crystallises in a cubic lattice, and the edge of a unit cell is 430 pm. The density of sodium is 0.963 g/cm³, the atomic weight of sodium is 23.0. How many atoms of sodium are contained in one unit cell? What type of cubic unit cell does sodium form?

Solution. The edge of the unit cell is 4.30×10^{-8} cm. The volume of the unit cell, therefore, is $(4.30 \times 10^{-8}\ \text{cm}),^3$ or $7.95 \times 10^{-23}\ \text{cm}^3$. We must find the number of Na atoms in this volume.

We derive our conversion factors from the density of Na.

$$0.963\ \text{g Na} = 1\ \text{cm}^3$$

and the fact that 1 mol of Na (which is 23.0 g of Na) contains Avogadro's number of Na atoms.

$$6.02 \times 10^{23}\ \text{atoms Na} = 23.0\ \text{g Na}$$

$$\therefore \text{Atoms of Na} = 7.95 \times 10^{-23}\ \text{cm}^3 \left(\frac{0.963\ \text{g Na}}{1\ \text{cm}^3}\right) \left(\frac{6.02 \times 10^{23}\ \text{atoms Na}}{23.0\ \text{g Na}}\right)$$

$$= 2.00\ \text{atoms Na.}$$

Sodium crystallises in a body centred cell since the body centred cubic unit cell contains 2 atoms.

Problem 7.11. In an X-ray diffraction study of a crystal of barium using *X*-radiation of wavelength 229 pm gives a first order reflection at 27°8′. What is the distance between the diffracted planes?

Solution. Using Bragg equation

$$n\lambda = 2d.\ \sin\theta$$

$$n = 1;\ \lambda = 229\ \text{pm}$$

$$\theta = 27°8'$$

$$\therefore d = \frac{1 \times 229}{2 \times \sin 27°8'}$$

$$d = 251\ \text{pm}$$

Problem 7.12. In a crystalline solid *MX*, the first order reflections from (100), (110), and (111) faces using monochromatic X-rays are 8.4° and 5.2° respectively. How do the spacings of the three planes vary in the solid *MX*?

Solution. According to Bragg's law we have

$$2d\ \sin\theta = n\lambda$$

For a first order reflection, $n = 1$

$$d_{100} = \frac{\lambda}{2\ \sin 5.9°} = \frac{1}{0.103}$$

$$d_{110}=\frac{\lambda}{2\sin 8.4^\circ}=\frac{1}{0.146}$$

$$d_{111}=\frac{\lambda}{2\sin 5.2^\circ}=\frac{1}{0.0906}$$

$$d_{100}:d_{110}:d_{111}=\frac{1}{0.103}:\frac{1}{0.146}:\frac{1}{0.0906}$$

$$=1:0.705:1.14.$$

Problem 7.13. The element chromium exists as a body centred cubic lattice whose unit cell edge is 2.88 Å. The density of chromium is 7.20 g/c.c. How many atoms does 52.0 g of chromium contain?

Solution. The volume of the unit cell of chromium

$$=(2.88\ A)^3$$

$$=23.9\ A^3$$

$$\text{Volume of 52.0 g of chromium}=\frac{52.0\text{ g}}{7.20\text{ g/c.c.}}$$

$$=7.22\text{ cm}^3.$$

$$\text{The number of unit cells in this volume}=\frac{7.22\text{ cm}^3}{23.9\text{ A}^3\text{/unit cell}}$$

$$=3.02\times10^{23}\text{ unit cells}$$

Since each body centred cube has 2 atoms, the total number of atoms is $\frac{2\text{ atoms}}{\text{unit cell}}\times3.02\times10^{23}$

$$=6.04\times10^{23}\text{ atoms.}$$

Problem 7.14. The edge of the unit cell of KCl is 6.29×10^{-10} m, and the density of KCl is 1.99×10^{-3} kg m^{-3}. If the KCl unit cell is face centred cubic and contains 4K$^+$ ions and 4Cl$^-$ions per unit cell, then calculate the number of K$^+$ions in one kg of KCl.

Solution. Since the edge of the unit cell$=6.29\times10^{-10}$ m

The volume of the unit cell$=(6.29\times10^{-10})^3$ m^3

Further the density of KCl$=1.99\times10^3$ kg m^3

∴ Weight of the one unit cell$=1.99\times10^3\ (6.29\times10^{-10})^3$ kg

$$\therefore\ 1\text{ kg of KCl contains}=\frac{1}{(6.21\times10^{-10})^3\times1.99\times10^3}\text{ unit cells}$$

Since each unit cell contains 4K$^+$ions, therefore, the number of K$^+$ ions present per kg of KCl

$$=4\times\frac{1}{(6.29\times10^{-10})^3\times1.99\times10^3}$$

$$=8.07\times10^{27}.$$

EXERCISES

7.1. Classify the following unit cells in their proper crystal systems:

(*i*) $a=b=7.36\text{Å}$, $c=12.45\text{Å}$, $\alpha\neq\beta\neq\gamma$.

(*ii*) $a=4.47\text{Å}$, $b=7.64\text{Å}$, $c=11.32\text{Å}$, $\alpha=\gamma=90°$, $\beta=108°$.

(*iii*) $a=6.39\text{Å}$, $b=7.04\text{Å}$, $c=10.13\text{Å}$, $\alpha=\beta=\gamma=90°$.

(*iv*) $a=b=c=9.43\text{Å}$, $\alpha=\beta=\gamma=82°$.

[Ans. (*i*) triclinic, (*ii*) monoclinic, (*iii*) orthorhomic, (*iv*) rhombohedral.]

7.2. The volume of a general parallelopiped with sides *a*, *b* and *c* and angles α between *b* and *c*; β between *a* and *c*; γ between *a* and *b* is

$$V=abc(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\,\cos\beta\,\cos\gamma)^{\frac{1}{2}}.$$

Use the above formula along with the following data to calculate the number of molecules per unit cell in S_4N_4. Unit cell: monoclinic; $a=8.75\text{Å}$, $b=7.16\text{Å}$, $c=8.65\text{Å}$, $\beta=92.5°$. Density=2.20 g/cm^3 (experimental).

[Ans. 4]

7.3. The space group of $Cu_2[Cr(CN)_6]$ is Fm 3m and $a=10.24\text{Å}$. Assuming the value of $\lambda=1.5405\text{Å}$, calculate θ for the following planes:

(*i*) (1 2 0)

(*ii*) (1 3 2)

[Ans. 9°40′.]

7.4. A primitive unit cell has $a=5.00\text{Å}$, $b=6.00\text{Å}$, $c=7.00\text{Å}$, and $\alpha=\beta=\gamma=90°$. A new unit cell is chosen with edges defined by the vectors from the origin to the points with coordinates 3, 1, 0; 1, 2, 0 and 0, 0, 1.

(*i*) Calculate the volume of the original unit cell.

(*ii*) Calculate the lengths of the three edges and the three angles of the new unit cell.

(*iii*) Calculate the volume of the new unit cell.

[Ans. (*i*) 210Å^3; (*ii*) $a=16.16\text{Å}$, $b=13.00\text{Å}$, $c-7.00\text{Å}$
$\alpha=90°$, $\beta=90°$, $\gamma=45.6°$; (*iii*) 1050Å^3.]

7.5. Calculate the number of formula units in each of the following types of unit cells (*i*) ZnS in a zinc blend unit cell; (*ii*) nickel in a face centred cubic unit cell; (*iii*) MgO in a rock salt unit cell.

[Ans. (*i*) 4, (*ii*) 4, (*iii*) 4.]

7.6. Silver iodide crystallizes in the ccp zinc blend structure. Assuming that the iodide ions are located at the lattice, what fraction of the tetrahedral sites are occupied by the silver ions?

[Ans. Half.]

7.7. A unit cell has dimensions $a=6.00\text{Å}$, $b=7.00\text{Å}$, $c=8.00\text{Å}$, $\alpha=90°$, $\beta=115.0°$, $\gamma=90°$. Calculate the distance between the points 0.200, 0.150, 0.333 and 0.300 and 0.050, −0.123.

[Ans. 4.00Å.]

7.8. Calculate the value of Avogadro's number from the distance between the centres of adjacent ions in NaCl, 2.82Å, and density of solid, 2.17 g/ml.

[Ans. 6.02×10^{23}.]

7.9. A rhombohedral unit cell has $a=6.00\text{Å}$, $\alpha=60.0°$. Show that a face centred cubic lattice may be chosen and calculate the dimension of the cubic cell. What is the criterion for deciding the classification of the crystal as cubic or rhombohedral?

[Ans. $a=8.48\text{Å}$. The classification is based on symmetry. A cubic crystal has four three-fold axes of symmetry, whereas a rhombohedral crystal has one axis of three-fold symmetry.]

7.10. A rhombohedral unit cell has $a=5.00\text{Å}$, $\alpha=75.0°$. (*i*) Calculate the volume of rhombohedral cell. (*ii*) Calculate the volume of hexagonal cell from its dimensions. **[Ans.** (*i*) 114.13Å^3, (*ii*) 34.24Å^3.]

7.11. Calculate the θ values at which the following reflections would appear from a monoclinic, crystal with $a=5.50\text{Å}$, $b=8.50\text{Å}$, $c=7.08\text{Å}$, $\beta=110.0°$. (*a*) 010, (*b*) 020, (*c*) 321, (*d*) 321. Assume an X-ray wavelength of 1.542Å. **[Ans.** (*a*) 5.50°, (*b*) 11.04°, (*c*) 27.7°, (*d*) 32.0°.]

7.12. Calculate the density of solid Krypton at 58 K. The solid Krypton has a cubic close packed structure with cell dimension 5.721Å. **[Ans.** 2.972 g/ml.]

7.13. Calculate the electron affinity of iodine, given the following data:

$U_{\text{NaI}} = -165.4$ k.cal. mole^{-1}

$\Delta H_{f\text{NaI}} = -64.8$ k.cal. mole^{-1}

$\Delta H_{\text{sub Na}} = 25.9$ k.cal. mole^{-1}

$I_{\text{Na}} = 118.4$ k.cal. mole^{-1}

$\frac{1}{2}(\Delta H_{\text{sub}(\text{I}_2)} + \Delta H_{\text{diss}(\text{I}_2)}) = 25.5$ k.cal. mole^{-1}

[Ans. 73.2 k cal. mole^{-1}]

7.14. Calculate the efficiency of packing for the hexagonal closed packed structure. **[Ans.** 74.05 per cent.]

7.15. Prove that $\frac{c}{a} = 2\sqrt{2}/\sqrt{3}$ for the hexagonal closed packed structure.

7.16. Calculate the efficiency of packing in the body-centred cubic structure. **[Ans.** 0.6802 or 68.2 per cent.]

7.17. Calculate the efficiency of packing in the diamond structure. The unit cell dimension of diamond is 3.567Å. **[Ans.** 0.3401.]

7.18. Copper crystallizes in a face-centred cubic lattice. The density of copper is 8.93 g/cm^3. What is the length of the edge of unit cell? **[Ans.** 3.62Å.]

7.19. Aluminium crystallizes in a face-centred cubic unit cell with the length of an edge equal to 4.05Å. Assume that atoms are identical hard spheres and that a face-centred atom touches each of the four atoms of its face: (*a*) Calculate the length of the diagonal of a face, (*b*) calculate the radius of the hard sphere atoms comprising the crystal using the length of the diagonal of a face obtained in (*a*). **[Ans.** (*a*) 5.71Å, (*b*) 1.43Å.]

7.20. Platinum crystallizes in the face-centred cubic structure with $a=3.923\text{Å}$. Calculate the theoretical density of platinum. **[Ans.** 21.5×10^3 kg m^{-3}.]

7.21. Calculate the theoretical density of rhombic sulphur if $a=10.4646\text{Å}$, $b=12.8660\text{Å}$ and $c=24.4860\text{Å}$, $Z=128$ for this unit cell. **[Ans.** 2.067×10^3 kg m^{-3}.]

7.22. The metal nickel crystallizes in a face-centred cubic structure. Its density is 8.90 g/c.c. Calculate (*i*) the radius of a nickel atom, (*ii*) the length of the edge of a unit cell, and (*iii*) what volume do they occupy? **[Ans.** (*i*) 1.24Å, (*ii*) 3.52Å, (*iii*) 4.38×10^{-23} cm^3.]

7.23. An X-ray from a copper target of wevelength 1.5374Å is reflected from two parallel planes 2.82Å apart. What is the angle of reflection for $n=1$? **[Ans.** 15.8°.]

7.24. Prove that in the cubic closest packed structure, the empty space is 25.9 per cent. Estimate the percentage empty space in a body-centred cubic structure. **[Ans.** 31.98 per cent.]

7.25. Metallic gold crystallizes in a face-centred cubic structure which is 4.078Å on an edge. The density of gold is 19.30 g/cm^3 at 25°C. Calculate (*i*) the atomic radius of gold, and (*ii*) Avogadro's number.

[Ans. 1.442Å, 6.020×10^{23}.]

7.26. Rubidium iodide (RbI) crystallizes in a body-centred cubic structure radius with each Rb^+ ion surrounded by 8I^- ions and *vice-versa*. The ionic radius of Rb^+ is 1.49Å and the ionic radius of I is 2.17Å. Find the length of one side of RbI unit cell.

[Ans. 4.23Å.]

8

CHEMICAL EQUILIBRIUM

Law of Mass Action

The law of mass action was given by Guldberg and Waage in 1864. It states that at constant temperature, the rate at which a substance reacts is directly proportional to the active mass. The velocity of a chemical reaction is directly proportional to the product of the active masses of reactants. Alternatively it may be postulated that the rate of a chemical reaction is proportional to the molar concentration of the reacting substances. Equilibrium may be the most important concept in chemistry. In principle most chemical reactions are reversible. The reversible reactions can best be understood in terms of the concept of chemical equilibrium. Consider a general reaction $A \rightarrow B$. The rate of the reaction depends upon the amount of A available. If the reaction is reversible, then $A \leftarrow B$ will also occur, and the rate of reaction will depend upon the concentration of B available. As the forward reaction $A \rightarrow B$ proceeds, the concentration of A decreases and the concentration of B increases, so does the rate of reverse reaction. At equilibrium the rates of forward and reverse reactions become equal.

For the reaction,

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant is

$$K = \frac{[C]^c\ (D]^d}{[A]^a\ [B]^b} \qquad \ldots (1)$$

The square brackets indicate equilibrium concentrations in moles per litre. In the generalized equation (1) we see that the numerator is the product of equilibrium concentrations of the substances formed, each raised to the power equal to the number of moles of that substance in the chemical equation. The denominator is again the product of the equilibrium concentrations of the reacting substances, each raised to the power equal to the number of moles of the substance in the equilibrium equation. The quotient of these two is constant, called equilibrium constant.

The free energy change ΔG° in a reaction is related to the thermodynamic equilibrium constant K_a for the reaction,

$$\Delta G^\circ = -RT \ln K_a \qquad \ldots (2)$$

Relation between K_p and K_c. The equilibrium constant expressed in terms of pressures K_p is related to K_c the concentration equilibrium constant by the relation,

$$K_p = K_c\,(RT)^{\Delta n}$$

where Δn=number of moles of gaseous products—number of moles of gaseous reactants, R is a gas constant and T is the temperature in Kelvin.

Le Chatelier's principle states that when a constraint is placed on a system, at equilibrium, the equilibrium shifts in such a way as to tend to annual that constraint. The novel constraints are pressure or volume changes, temperature changes and the addition of constituents.

(*i*) **Effect of pressure changes.** Consider the following equilibrium at constant temperature

$$\underset{\substack{\text{2 molecules}\\ \text{2 volumes}}}{2NO_2} \rightleftharpoons \underset{\substack{\text{2 molecules}\\ \text{2 volumes}}}{2NO} + \underset{\substack{\text{1 molecule}\\ \text{1 volume}}}{O_2}$$

On increasing the pressure the equilibrium will move to the left in order to decrease the volume of the system and so minimise the effect of increased pressure. The reverse will apply if the pressure is decreased.

(*ii*) **Effect of temperature changes.** Consider the following equilibrium at constant pressure

$$C + H_2O\,(g) \rightleftharpoons CO + H_2 \quad \Delta H = +X \text{ joules}$$

The forward reaction is endothermic (heat is absorbed) and the reverse reaction is, therefore, exothermic (heat is evolved). If the temperature is increased the equilibrium will move to the right in an attempt to annual the constraint. Thus higher the temperature, the higher the proportions of hydrogen and carbon monoxide at equilibrium.

(*iii*) **Effect of adding more of one constituent.** Consider the following system at equilibrium at constant temperature and pressure

$$2SO_2 + O_2\,(\text{air}) \rightleftharpoons 2SO_3$$

If excess of air is now added, the equilibrium will move so as to oppose this addition by removing some of the oxygen on combination with sulphur dioxide to form sulphur trioxide. A higher percentage conversion of sulphur dioxide to sulphur trioxide is thus achieved.

A catalyst does not alter the position of equilibrium, but it greatly increases the speed with which equilibrium is attained. This is because a catalyst not only increases the forward and reverse reaction rates, but increases them to the same extent.

Problem 8.1. A mixture of CO(g) and Cl_2(g) are placed in a one litre container where they react to form $COCl_2$(g). When equilibrium is reached, analysis shows there are 0.30 mole of CO, 0.20 mole of Cl_2 and 0.80 mole of $COCl_2$, in the container. Calculate the equilibrium constant for the reaction.

$$CO(g)+Cl_2(g) \rightleftharpoons COCl_2(g)$$

Solution. The equilibrium constant K for this reaction can be written as

$$K=\frac{[COCl_2]}{[CO]\,[Cl_2]}$$

$$K=\frac{[0.80]}{(0.30)\,(0.20)}$$

$$K=13.3.$$

Problem 8.2. For the reaction

$$d \rightleftharpoons e+f$$

the equilibrium constant is 5.0×10^{-5} mole/litre at 25°C. A solution which is 1.0×10^{-4} molar in d is allowed to equilibrate at 25°C. What would be the equilibrium concentration of f?

Solution. Let x be the concentration of f at equilibrium. Since one mole of f is produced for every mole of e, the equilibrium concentration of both e and f will be x, and the equilibrium concentration of d will be $[d^\circ-x]$

$$K=\frac{[e]\,[f]}{[d]}$$

$$K=\frac{[x]\,[x]}{[d^\circ-x]}$$

$$\frac{x^2}{[d^\circ-x]}=5.0\times10^{-5}$$

$$\frac{x^2}{(1.0\times10^{-4}-x)}=5.0\times10^{-5}$$

$$x^2+5.0\times10^{-5}\,x-5.0\times10^{-9}=0$$

$$x=[e]=[f]=5.0\times10^{-5}\,M.$$

Problem 8.3. Ammonia dissolves and reacts with water. The following equilibrium is set up:

$$NH_3(aq)+H_2O \rightleftharpoons NH_4^+\,(aq)+OH^-\,(aq)$$

When ammonium ion is added (in the form of ammonium chloride), what will happen to the mass of hydroxide ion in solution?

(*i*) It will increase.

(*ii*) It will remain the same.

(*iii*) It will decrease.

(*iv*) It is not possible to say without more information.

Solution. The addition of ammonium chloride results in an increase in concentration of NH_4^+ (aq). The equilibrium automatically adjusts itself to nullify this change. The NH_4^+ (aq) concentration is reduced by combination with OH^- (aq) to form NH_3 (aq)$+H_2O$. Hence (*iii*) is correct.

Problem 8.4. For the reaction

$$Zn+2HCl \rightarrow ZnCl_2+H_2$$

$\triangle H$ is negative. At 20°C using 2M HCl, 20 cm^3 of gas are released every minute. Explain why the rate of production of hydrogen increases when this is done at a higher temperature?

Solution. For the reaction at equilibrium

$$A+B \rightleftharpoons C+D$$

the reaction is exothermic from left to right. Increasing the temperature will result in more of A and B in the equilibrium mixture. The reaction $Zn+2HCl \rightarrow ZnCl_2+H_2$ is exothermic, yet increasing the temperature appears to increase the amount of the product! This system is not at equilibrium. The increase of temperature can only speed the forward reaction rate. No backward reaction is possible as $H_2(g)$ is escaping.

Problem 8.5. For the dissociation of water, $H_2O(g) \rightleftharpoons H_2(g)+\frac{1}{2}O_2(g)$ at 500°C, the value of K_p with partial pressures in atmospheres is 1.87×10^{-6}. Assuming the ideal gas behaviour of gases, calculate the corresponding value of K_c with concentration in moles per litre.

Solution. For the reaction, $H_2O(g) \rightleftharpoons H_2(g)+\frac{1}{2}O_2(g)$.

$$\triangle n = 3/2-1=0.5$$

$$T = 500+273=773 \text{ K}$$

$$R = 0.082 \text{ litre atm deg}^{-1} \text{ mole}^{-1}$$

$$K_p = K_c\,(0.082\times773)^{0.5}$$

$$K_c = \frac{1.87\times10^{-6}}{(0.082\times773)^{1/2}}$$

$$K_c = 2.35\times10^{-7}.$$

Problem 8.6. If 1.588 g of nitrogen tetraoxide gives a total pressure of 760 torr when partially dissociated in a 500 cm^3 glass vessel at 25°. What is the degree of dissociation, α ? What is the value of K_p? What is the degree of dissociation at a total pressure of 0.5 atm?

Solution. $M = \frac{RTg}{PV} = \frac{(0.08205 \times 298 \times 1.588)}{(1 \times 0.500)}$

$$M = 77.68 \text{ mole}^{-1}$$

$$\alpha = \frac{92.02 - 77.68}{77.68} = 0.1846$$

$$K_p = \frac{4\alpha^2 P}{1-\alpha^2} = \frac{4\ (0.1846)^2\ (1)}{1-(0.1846)^2} = 0.141$$

The degree of dissociation at a total pressure of 0.5 atm

$$K_p = 0.141 = \frac{4\alpha^2\ (0.5)}{1-\alpha^2}$$

$$0.141\ (1-\alpha)^2 = 2$$

$$\alpha = 0.257.$$

Problem 8.7. At a certain temperature, $K=0.051$ for the reaction

$$CO(g)+H_2O(g) \rightleftharpoons CO_2+H_2(g)$$

In an experiment, the system is at equlibrium with, $CO_2(g)=0.90$, $H_2=0.90$, $[CO]=4.0$, and $[H_2O]=4.0$. An additional 1.0 mole per litre of CO and H_2O are added to the container. Find the concentrations of CO, H_2O, CO_2 and H_2 when the system again reaches equilibrium.

Solution.

$$\text{Equilibrium constant } K = \frac{[CO_2]\ [H_2]}{[CO]\ [H_2O]}$$

$$K = \frac{0.90 \times 0.90}{4.0 \times 4.0}$$

$$K = 0.051.$$

On adding additional 1.0 mole per litre of CO and H_2O we make $[CO]=5.9$ and $[H_2O]=5.0$. In order for the equilibrium expression to remain constant the numerator must get larger, the denominator gets smaller or both. This is achieved by shifting the equilibrium to the right i.e., some CO and H_2O will react to form CO_2 and H_2O until the ratio is again 0.51. Let the concentration of CO_2 formed be X, then the concentration of H_2 formed will also be X. The concentrations of CO and H_2O used up would also be X. Thus in the reaction

$$CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$$

$$(5.0-X)(5.0-X)\ (0.90+X)(0.90+X)$$

$$K = \frac{[CO_2]\ [H_2]}{[CO]\ [H_2O]} = \frac{(0.90+X)\ (0.90+X)}{(5.0-X)\ (5.0-X)}$$

$$K = 0.051$$

$$X = 0.20.$$

So, when equilibrium is established, $[CO_2]=[H_2]=0.90+0.20=1.10$ and $[CO]=[H_2O]=5.0-0.20=4.80$.

Problem 8.8. The reaction $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$ has an equilibrium constant of 6.0 at a certain temperature. If the system is equilibrated at $[H_2]=0.50$, $[I_2]=0.50$ and $[HI]=1.23$ in a one litre flask and suddenly 0.60 mole of HI is removed. What will be the concentrations of all species when equilibrium is re-established?

Solution. $H_2+I_2 \rightleftharpoons 2HI$

$$\frac{[HI]^2}{[H_2]\,[I_2]}=K=6.0$$

On removal of HI equilibrium will be shifted to the right using up some H_2 and I_2 to form HI until equilibrium is reached. Immediately upon removal of 0.60 mole of HI, we are left with $[H_2]=[I_2]=0.50$ and $[HI]=0.63$. Let X be the moles per litre of H_2 that react, when equilibrium is reached, $[H_2]=(0.50-X)$. One I_2 reacts for every H_2 that reacts, so we will also have $[I_2]=(0.50-X)$. For each H_2 or I_2 used two HI are formed, so at equilibrium $[HI]=(0.63+2X)$

$$\frac{(0.63+2X)^2}{(0.50-X)\,(0.5-X)}=6.0$$

$$X=0.135 \simeq 0.14$$

So, when equilibrium is re-established, $[H_2]=[I_2]=(0.50-0.14)=0.36$, and $[HI]=(0.63+2\times 0.14)=0.91$.

Problem. 8.9. The equilibrium constant for the reaction

$$A+B \rightarrow C+D$$

at 25°C is 2.0×10^{10}. What is the standard free energy change for this reaction?

Solution. $\Delta G^\circ=-2.303\ RT \log K_a$

$$\Delta G^\circ=-2.303\ (2.0\ \text{cal./deg})\ (298)\ \log 2.0\times 10^{10}$$

$$\Delta G^\circ=-(2.303)\ (2.0)\ (298)\ (10.3)$$

$$\Delta G^\circ=-14{,}000\ \text{cal.}$$

$$\Delta G^\circ=\ 14\ \text{k.cal.}$$

Problem 8.10. At 298 K, the equilibrium constant and ΔH° for the reaction

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

are 8.8 and -13.9 k.cal, respectively. What is the value of the equilibrium constant at 273 K?

Solution. $\log \dfrac{K_2}{K_1}=\dfrac{-\Delta H^\circ}{2.3\ R}\left(\dfrac{1}{T_2}-\dfrac{1}{T_1}\right)$

$K_1=8.8,\qquad \Delta H^\circ=-13.9$ k.cal.

$T_1=298,\qquad T_2=273$

$$\log\frac{K_2}{8.8}=\frac{-(-13{,}900)}{2.3\times 2.0}\left(\frac{1}{273}-\frac{1}{298}\right)$$

$$K_2=7.1.$$

Problem 8.11. The equilibrium constant for the reaction

$$2HI(g)=H_2(g)+I_2(g)$$

s 2.18×10^{-2} at 764 K and is 1.64×10^{-2} at 667 K. Calculate ΔH° for the reaction.

Solution. $\log\frac{K_2}{K_1}=\frac{-\Delta H^\circ}{2.3\,R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

$$\log\frac{2.18\times 10^{-2}}{1.64\times 10^{-2}}=\frac{-\Delta H^\circ}{2.3\times 2.0}\left(\frac{1}{764}-\frac{1}{667}\right)$$

$$\Delta H=3000 \text{ cal.}$$

Problem 8.12. The equilibrium constant at 25°C for the reaction $N_2O_4 \rightleftharpoons 2NO_2(g)$ is $K_p=0.113$ atm. Determine the partial pressure of $NO_2(g)$ in a system under a total pressure of 1.0 atm when 0.050 moles of $N_2O_4(g)$ are sealed in a container and allowed to come to equilibrium at 25°C.

Solution. $K_p=\frac{4x^2\,P_T}{(a-x)\,(a+x)}$

$$K_p=\frac{4x^2\,P_T}{a^2-x^2}$$

$$0.113=\frac{4x^2\,(1.0)}{(0.050)^2-x^2}$$

$$4.113x^2=2.83\times 10^{-4}$$

$$x=8.29\times 10^{-3}$$

$$P_{NO_2}=\left(\frac{2}{a+x}\right)P_T$$

$$P_{NO_2}=\frac{2(8.29\times 10^{-3})(1.0)}{0.050+8.29\times 10^{-3}}$$

$$P_{NO_2}=0.284 \text{ atm.}$$

Problem 8.13. The equilibrium constant K_p for the reaction

$$NH_3(g) \rightleftharpoons \tfrac{1}{2}N_2(g)+\tfrac{3}{2}H_2(g)$$

is 1.22×10^{-3} at 298.2 K. Determine K_p for the reaction at 498.2 K given that $\Delta H^\circ=46{,}190$ J.

Solution. $\log\frac{Kp_1}{Kp_1}=-\frac{\Delta H^\circ}{2.303\,R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

$$\log\frac{Kp_2}{1.22\times 10^{-3}}=\frac{46{,}190}{(2.303)\,(8.314)}\left(\frac{1}{498.2}-\frac{1}{298.2}\right)$$

$$\frac{K_{P2}}{1.22\times10^{-3}}=1.77\times10^{3}$$

$$K_{P2}=2.16.$$

Problem 8.14. The value of K for the reaction $N_2+3H_2 \rightleftharpoons 3NH_3$ is 6.4×10^{-2} at 500°C. Calculate the equilibrium concentrations of each of the component if the starting amounts are 1.00 mole of nitrogen and 1.00 mole of hydrogen in a 2.00 litre flask at 500°C.

Solution. $[N_2]_{start}=\dfrac{1.00 \text{ mole}}{2.000\ l}=0.500 \text{ mole}/l$

$$[H_2]_{start}=\frac{1.000 \text{ mole}}{2.000\ l}=0.500 \text{ mole}/l$$

Let x be the equilibrium concentration of NH_3, we can obtain the equilibrium concentrations of N_2 and O_2 in terms of x and the starting concentration. According to the chemical reaction $\frac{1}{2}$ mole of N_2 and $\frac{3}{2}$ moles of H_2 are needed to produce 1 mole of NH_3 i e.,

$$[N_2]_{eq}=(0.500-0.5x) \text{ mole}/l$$
$$[H_2]_{eq}=(0.500-1.5x) \text{ mole}/l$$
$$[NH_3]_{eq}=x \text{ mole}/l$$

On substituting the values of the equilibrium concentrations of H_2, N_2 and NH_3 in the equilibrium constant,

$$K=\frac{[NH_3]^2_{eq}}{[N_2]_{eq}\,.\,[H_2]^3_{eq}}=\frac{x^2}{(0.500-0.50x)(0.500-1.5x)^3}$$

$$K=6.4\times10^{-2}$$

The solution of the equation gives the value of x,

$$x=4.9\times10^{-2} \text{ mole}/l=NH_3 \text{ concentration}$$

$[N_2]=0.500-0.5x=0.500-0.024=0.476$ mole/l

$[H_2]=0.500-1.5x=0.500-0.073=0.427$ mole/l

Problem 8.15. The partial pressures of gaseous CO, Br_2 and $COBr_2$ in the equilibrium $CO(g)+Br_2 \rightleftharpoons COBr_2(g)$ were found to be 0.222 atm, 0.124 atm and 0.086 atm at 35°C. Calculate K_p and K_c for the equilibrium, and comment on the effect of pressure on equilibrium composition.

Solution. $K_p=\dfrac{P_{COBr_2}}{P_{CO_2}\,.\,P_{Br_2}}$

$$K_p=\frac{0.086}{0.222\times0.124}$$

$$K_p=3.62 \text{ atm}^{-1}$$

$$K_p=K_C(RT)^{\Delta n}$$

$$K_p=K_C(RT)^{-1}$$

$$K_C = \frac{K_p}{(RT)^{-1}}$$

$$K_C = \frac{3.62}{0.0821 \times 308}$$

$$K_C = 0.143 \text{ litre mole}^{-1}.$$

The increase of pressure will favour the formation of $COBr_2$ because there is a decrease in volume in this reaction.

Problem 8.16. For the reaction

$$3Fe_2O_3(s) \rightleftharpoons 2Fe_3O_4 + \tfrac{1}{2}O_2(g)$$

$$\triangle H^\circ_{298} = 55.5 \text{ k.cal.} \quad \text{and} \quad \triangle G^\circ_{298} = 46.5 \text{ k.cal.}$$

(*a*) Calculate the equilibrium constant K_p at 25°C for this reaction.

(*b*) Calculate the equilibrium constant for this reaction at 125°C.

Solution. (*a*) $\triangle G^\circ_{298} = 46.5$ k.cal.

$$\log K_p = -\frac{\triangle G^\circ}{2.303\ RT} = -\frac{46.5}{2.303 \times 1.987 \times 10^{-3} \times 298.15}$$

$$\log K_p = -34.1$$

$$K_p = 8 \times 10^{-35}$$

(*b*) $\triangle H^\circ_{298} = 55.5$ k.cal.

$$\log K_{T_2} = \log K_{T_1} + \frac{1}{2.303\ R}\int_{T_1}^{T_2} \frac{\triangle H^\circ}{T_2}\ .\ dT$$

$$\log K_{T_2} = \log K_{T_1} + \frac{\triangle H^\circ (T_2 - T_1)}{2.303\ RT_1\ T_2}.$$

$$\log K_{398} = -34.1 + \frac{55.5 \times 100}{2.303 \times 1.987 \times 10^{-3} \times 298.15 \times 398.15}$$

$$K_{398} = 1.3 \times 10^{-24}.$$

Problem 8.17. Standard free energies of formation of ethyl *n*-butyrate and *n*-butyric acid, water and ethanol at 25°C are —76.0, —91.5 k. cal. —56.69 and —41.63 k. cal. respectively. How much ether is formed when 0.5 mole of *n*-butyric acid is mixed with 2 mole of ethanol and allowed to come to equilibrium at 25°C?

Solution. The chemical reaction is,

$$CH_3CH_2CH_2COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3CH_2COOC_2H_5(l) + H_2O(l)$$

$$\triangle G^\circ = (-76.0 - 56.69) - (-91.5 - 41.63)$$

$$= +0.440 \text{ k.cal.}$$

Since $\triangle G^\circ = -RT\ lnK$

$$= -2.303\ RT \log K$$

$$\log K = -\frac{\triangle G^\circ}{(2.303)(1.987)(298)}$$

$$\log K = -\frac{0.440}{(2.303)(1.987)(298)}$$
$$= -0.323$$
$$K = 0.48.$$

Also

$$K = \frac{y^2}{(0.5-y)(2-y)}$$
$$0.52y^2 + 1.20y - 0.48 = 0$$

The positive root of this equation has a value 0.35 mole.

EXERCISES

8.1. Which of the following are equilibrium situations and which are steady state situations?

(*i*) A well-fed lion in a cage. The lion's weight is constant.

(*ii*) The liquid mercury and mercury vapour in a thermometer. Temperature is constant.

(*iii*) A playing basketball team and the bench of reserves. The number of "players in the game" and the number "on the bench" are constant.

[Ans. (*ii*) and (*iii*) are equilibrium situations.]

8.2. Methanol is made according to the following equation

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) + \text{heat}$$

Predict the effect on equilibrium concentrations, of an increase in (*a*) temperature, (*b*) pressure.

[Ans. (*a*) Decreases CH_3OH, (*b*) Increases CH_3OH.]

8.3. Given

$$SO_2(g) + O_2(g) \rightleftharpoons SO_3(g) + 23 \text{ k. cal.}$$

(*a*) For this reaction discuss the conditions that favour a high equilibrium concentration of SO_3.

(*b*) How many grams of oxygen gas are needed to form 1.00 gm of SO_3?

[Ans. 0.200 gram of O_2.]

8.4. Select from each of the following pairs the more random system:

(*a*) A brand new deck of cards arranged according to suit any number.

(*a'*) The same deck of cards after shuffling.

(*b*) A box full of sugar cubes.

(*b'*) Sugar cubes thrown on the floor.

(*c*) A hay stack.

(*c'*) Stacked fire wood. [Ans. (*a'*), (*b'*) and (*c'*).]

8.5. At 248°C and 1 atm pressure $\alpha = 0.718$ for the dissociation

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

Calculate K_p for the reaction. [Ans. $K_p = 1.07$.]

8.6. At 3000K and 1 atm, CO_2 is 40 per cent dissociated into CO and O_2 (*a*) what will be the degree of dissociation if the pressure is raised to 2 atm? (*b*) What will be the degree of dissociation when a mixture of 50 per cent CO_2 and 50 per cent O_2 is heated to 3000K, the pressure being 1 atm?

[Ans. (*a*) 0.335; (*b*) 0.271]

8.7. NH_4HS disociates as follows:

$$NH_4HS(s) \rightleftharpoons NH_3(g)+H_2S(g)$$

At 25°C the dissociation pressure of the pure solid is 500 mm Hg. Calculate (*a*) K_p and (*b*) the total pressure at equilibrium when 300 mm of NH_3 are introduced into a flask containing solid NH_4HS.

[Ans. (*a*) 6.25×10^4 mm^2 (*b*) 583.0 mm.]

8.8. When equilibrium is established in the reaction,

$$W+X \rightleftharpoons Y+Z$$

the percentage of each of the four constituents is constant. Among which are collisions occurring?

(*i*) *W*'s are colliding with *X*'s while *Y*'s are colliding with *Z*'s only.
(*ii*) *W*'s, *X*'s, *Y*'s and *Z*'s are colliding with each other.
(*iii*) *W*'s are colliding with *Z*'s while *X*'s are colliding with *Y*'s only.
(*iv*) Collisions between *W*'s and *X*'s, and between *Y*'s and *Z*'s are no longer occurring. [Ans. (*ii*).]

8.9. If $K=1.8$ for the reaction

$$N_2(g)+3H_2(g)\rightleftharpoons2NH_3(g),$$

how many moles of NH_3 must be placed in a 1.0 litre container in order to yield an equilibrium concentration for H_2 of 6.0 M? [Ans. 31.9.]

8.10. For the reaction

$$2SO_2(g)+O_2(g)\rightleftharpoons2SO_3(g),\ K=5.0\times10^3$$

at 500°C. The system is at equilibrium with $[SO_2]=1.0$, $[SO_3]=10.0$ and $[O_2]=0.02$. How many moles per litre of SO_3 must be added in order to make $[O_2]=1.02$ at equilibrium?

8.11. For the reaction $Cl_2(g)\rightleftharpoons2Cl(g)$, $K=3.6\times10^{-2}$ at 2000°C. How many moles of Cl_2 must be placed in a 3.0 litre container in order to yield 0.10 mole of atomic chlorine at equilibrium? [Ans. 0.092 mole.]

8.12. An equilibrium mixture $XeF_2(g)+OF_2(g)\rightleftharpoons XeOF_2(g)+F_2(g)$, was found to contain 0.60 mole of XeF_2, 0.30 mole of OF_2, 0.10 mole of $XeOF_2$ and 0.40 mole of F_2 in a one litre container. How many moles of OF_2 must be added to increase $[XeOF_2]$ to 0.20 M?

8.13. For the reaction $2a\rightleftharpoons c+d$,

the equilibrium constant is 1.0×10^{-3}. At equilibrium the concentrations observed were, $[c]=1.2\times10^{-3}$ M, $[d]=3.8\times10^{-6}$ M. What was the concentration of $[a]$ at equilibrium? [Ans. 2.1×10^{-3} M.]

8.14. A compound, HB, is formed from H and B according to the equation

$$H+B\rightleftharpoons HB.$$

A solution was prepared by dissolving 0.100 mole of H and 0.100 mole of B in enough water to make the total volume equal to one litre. After equilibrium had been established, it was found that 20 per cent of H had reacted. What are the equilibrium concentrations of H, B and HB? What is *K* for this reaction?

[Ans. [HB]=0.020 M, [H]=0.080 M, [B]=0.080 M, $K=3.1$ *l*/mole.]

8.15. All dissociation equilibria of the type $A_2(g)\rightleftharpoons2A(g)$ are shifted to the right at higher temperatures. How does thermodynamics explain this fact?

[Ans. ΔS is positive and $T\Delta S$ becomes larger in Gibbs-Helmholtz equation at higher temperatures.]

8.16. A solution is prepared by dissolving 0.10 mole of NH_3 gas in enough water to make 1.0 litre of solution. What is the $[OH^-]$ in the resulting solution?

[**Ans.** 1.3×10^{-3} M]

[**Hint.** $NH_3+H_2O\rightarrow NH_4OH$. K_{eq} for the reaction $NH_4OH\rightleftharpoons NH_4^++OH^-$ is 1.8×10^{-5} mole/l.]

8.17. When 2.94 moles of iodine and 8.1 moles of hydrogen are heated at constant volume at 444°C until equilibrium is established, 5.64 moles of hydroiodic acid are formed. Find the equilibrium constant. [**Ans** 50.2.]

8.18. Reactants P and Q are mixed, each at a concentration of 0.80 mole l^{-1}. They react to produce R and S. At equilibrium the concentration of R is found to be 0.60 mole l^{-1}. Calculate the value of equilibrium constant. The chemical reaction can be symbolised as under

$$P+Q\rightleftharpoons R+S$$

[**Ans.** 9.0.]

8.19. At 2000 K and 1 atm pressure $H_2O(g)$ is 1 per cent dissociated into $H_2(g)$ and $O_2(g)$. Calculate K_p for the reaction $2H_2O(g)\rightleftharpoons 2H_2(g)+O_2(g)$. [**Ans.** 5.084×10^{-7} atm.]

8.20. Predict the effect on each of the following equilibrium of decreasing the volume of the system

(*a*) $CaCO_3(s)\rightleftharpoons CaO(s)+CO_2(g)$ —heat

(*b*) $2C(s)+O_2(g)=2CO(g)$+heat [**Ans.** (*a*) left, (*b*) left.]

8.21. What is the effect on the following equilibrium if each of the indicated changes is made?

$$N_2(g)+2O_2(g)\rightleftharpoons 2NO_2(g)+\text{heat}$$

(*a*) increase in concentration of N_2, (*b*) decrease in temperature, (*c*) increase in volume, (*d*) decrease in O_2 concentration, (*e*) addition of a catalyst.

[**Ans.** (*a*) right, (*b*) right, (*c*) left, (*d*) left, (*e*) none.]

8.22. The equilibrium constant for the reaction $H_2(g)+I_2(g)\rightleftharpoons 2HI(g)$ is 64 at a certain temperature. If 12 g of hydrogen and 762 g of iodine be kept in a sealed vessel at this temperature the yield of HI is 0.02. Calculate the percentage of iodine converted into hydrogen iodide. [91.3 per cent.]

8.23. One gram of PCl_5 is sealed in an evacuated bulb, K_p for the dissociation of phosphorus pentachloride is 0.298 at 200°C. Calculate K_c for the dissociation at the same temperature. [Ans. 7.68×10^{-3}.]

8.24. Assuming that the degree of dissociation of PCl_5 at a certain temperature and under atmospheric pressure is 0.2, calculate the pressure at which it will be half dissociated at the same temperature. [**Ans.** 1.2×10^{-2} atm.]

8.25. At 800°C, under a total pressure of one atmosphere, PCl_5 is 50 per cent dissociated. Calculate K_p. What is the pressure under which it is 75 per cent dissociated under the same temperature? [**Ans.** 0.111 atm.]

8.26. The molecular weight of N_2O_4 at 30°C is 80, which differs from the value expected from the formula. What nature of the change does N_2O_4 undergo? Calculate the extent of the change. [**Ans.** $N_2O_4\rightleftharpoons 2NO_2$.]

8.27. One mole of PCl_5 was placed in a one litre vessel. At equilibrium, 0.20 mole of Cl_2 were found in the vessel. Find the equilibrium constant for the reaction $PCl_5\rightleftharpoons PCl_3(g)+Cl_2(g)$. [**Ans.** 0.50.]

8.28. Exactly 3.0 moles of S_2Cl_4 are introduced into a five-litre container. The reaction $S_2Cl_4(g)\rightleftharpoons 2SCl_2(g)$ occurs, and at equilibrium only 0.20 mole of S_2Cl_4 remain in the container. Calculate the value of equilibrium constant K for the reaction. [**Ans.** 31.4.]

8.29. Consider the equilibrium, $2NO(g)+2CO(g)\rightleftharpoons 2CO_2(g)+N_2(g)$. When equilibrium is established, which way will it shift, if (*a*) CO_2 is added, (*b*) N_2 is removed, (*c*) NO is added, (*d*) the volume of the container is suddenly decreased? **[Ans. (*a*) left, (*b*) right, (*c*) right, (*d*) right.]**

8.30. A mixture containing 3 moles of acetic acid and one mole of ethyl alcohol was heated to equilibrium. Calculate the amount of ethyl acetate produced. The equilibrium constant for the reaction is 4.0. **[Ans. 69.56 g.]**

8.31. The equilibrium constant for the reaction

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

is 4.0. What will be the composition of the equilibrium mixture?

8.32. 2.0 g of ammonium chloride was heated in a one litre flask to 300°C. From the measurement of pressure it was found that 98 per cent of ammonium chloride was dissociated. If to this flask 2.0 g of dry ammonia was added, what would be the percentage dissociation? **[Ans. 9.126.]**

8.33. Reactants q and r form s according to the following equation

$$q + r \rightleftharpoons s.$$

The initial concentrations of q and r were 0.8 and 1.5 mole/litre respectively ($[s]=0$). At equilibrium the concentration of s was 0.3 mole/litre. What is the equilibrium concentration for the above reaction?

[Ans. 0.5 *l*/mole.]

8.34. What is the per cent dissociation of $NOCl(g)$ into $NO(g)$ and $Cl_2(g)$ at 1.00 atm and 10^{-3} atm if $\Delta G°$ (formation)=15.79 k. cal. mole^{-1} for $NOCl(g)$ and 20.69 k. cal. mole^{-1} for $NO(g)$? Assume ideal gas behaviour.

[Ans. $\Delta G°_{298}$ (reaction)=20.50 kJ for 1 mole $NOCl(g)$, $K=K_p=2.55\times10^{-4}$; 0.51 per cent and 4.93 per cent.]

8.35. Calculate the pressure of $CO_2(g)$ over a sample of $CaCO_3(s)$ at 1000 K if $\Delta G°_{1000}=22.90$ kJ for the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

[Ans. $K=K_p=a_{CO_2}=p_{CO_2}=6.39\times10^{-2}$ atm.]

8.36. Nitric acid in gaseous phase may decompose according to the equation

$$4HNO_3(g) \rightleftharpoons 4NO_2(g) + 2H_2O(g) + O_2(g)$$

If the reaction starts with pure HNO_3 prove that

$$K_P = \frac{1024\, P_{O_2}}{(P - 7P_{O_2})^4}$$

8.37. Calculate $\Delta G°_{298}$ for the reaction

$$Cu^{2+}(aq) + 4NH_3(aq) = [Cu(NH_3)_4]^{2+}(aq)$$

if $\Delta G°_{298} = -70.54$ kJ, $a_{Cu^{2+}} = 0.01$, $a_{NH_3} = 0.01$, $a_{complex} = 0.01$

[Ans. −24.89 kJ.]

8.38. If $\Delta°_{298} = -237.178$ kJ for the reaction

$$H_2(g) + O_2(g) = H_2O(l)$$

Calculate the value of K for this reaction. **[Ans. 3.7×10^{41}.]**

8.39. The temperature dependence of the standard Gibbs free energy for the reaction

$$Sb_2O_3(s) + 3CO(g) \rightleftharpoons 2Sb(l) + 3CO_2(g)$$

is given by the reaction

$$\Delta G° = -33{,}461 + 34.286T \log T - 11.1\times10^{-3}\,T^2 + 0.96\times10^{-6}\,T^3 - 88.65T$$

Calculate $\Delta G°_{1000}$ for the reaction

$$Sb_2O_3(s) \rightleftharpoons 2Sb(l) + \tfrac{3}{2}O_2(g)$$

if the Gibbs energies of formation of $CO_2(g)$ and $CO(g)$ at 1000 K are

$\Delta G_{f_{CO_2}} = -94{,}610$ cal. mole^{-1} and $\Delta G^\circ_{CO} = -47{,}942$ cal. mole^{-1}.

[Ans. 11.061 k. cal.]

8.40. For the reaction

$$CO(g)+H_2O(g)=CO_2(g)+H_2(g)$$

the equilibrium constant equals 4.0 at a given temperature. An amount of 0.5 mole of CO and 0.6 mole of steam were put into a 2 litre vessel at this temperature. Calculate the number of moles of CO_2 present at equilibrium.

[Ans. 0.4 mole.]

8.41. Consider the two gaseous equilibria involving SO_2 and the corresponding equilibrium constants at 25°C

$$2SO_2(g)+\tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \quad K_1$$

$$2SO_3(g) \rightleftharpoons 2SO_2(g)+O_2(g) \quad K_2$$

How are the equilibrium constants K_1 and K_2 related to each other?

$\left[\text{Ans. } K_2=\dfrac{1}{K_1{}^2}\right]$

8.42. Phosgene ($COCl_2$) is put into a two litre reaction vessel and then heated so that it is partially decomposed

$$COCl_2 \rightleftharpoons CO(g)+Cl_2(g)$$

At equilibrium the $COCl_2$ concentration was found to be 0.40 mole litre^{-1}. More $COCl_2$ was then added to the vessel and when the equilibrium was re-established, $[COCl_2]$ was found to be 1.6 moles litre^{-1}. How had the CO concentration changed?

[Ans. It was doubled.]

8.43. The equilibrium composition for the reaction below was found to be

$$CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$$

	CO(g)	H_2O(g)	CO_2(g)	H_2(g)
Equilibrium concentration (mole litre^{-1})	0.10	0.10	0.40	0.10

Then 0.30 mole of H_2 was added to the one litre reaction vessel. What was the new concentration of $CO_2(g)$ when the equilibrium was re-established?

[Ans. 0.33 mole litre^{-1}.]

8.44. Calculate the value of the equilibrium constant K for the reaction

$$2NO+O_2 \rightleftharpoons 2NO_2$$

if, after mixing 1.760×10^{-2} mole of NO and 9.0×10^{-3} mole of O_2 in a two litre flask at 250°C, it is found that the equilibrium concentration of NO is 8.0×10^{-4} mole/l.

[Ans. 2.0×10^{5} at 250°C.]

8.45. Consider the reaction $2X+Y=X_2Y$, all gases. Initially, 3 moles of X and 3 moles of Y are placed in a one litre container and after the reaction has attained equilibrium, 0.6 mole of X_2Y is present. (*a*) How many moles of X as such are present? (*b*) How many moles of Y are present? (*c*) Calculate the equilibrium constant.

[Ans. (*a*) 1.8 moles of X, (*b*) 2.4 moles of Y, (*c*) 7.7×10^{-2}.]

8.46. At 1273 K and a total pressure of 30 atm the equilibrium in the reaction $CO_2(g)+C(s)=2CO(g)$ is such that 17 mole per cent of the gas is CO_2. (*a*) What percentage would be CO_2 if the total pressure were 20 atm? (*b*) What would be the effect on the equilibrium of adding N_2 to the reaction mixture in a closed vessel until the partial pressure of N_2 is 10 atm? (*c*) At what pressure of the reactants will 25 per cent of the gas be CO_2?

[Ans. (*a*) 12.5 per cent, (*b*) No effect, (*c*) 54 atm.]

8.47. When platinum is heated in the presence of chlorine gas, the following reaction takes place

$$Pt(s)+Cl_2=PtCl_2(g)$$

At 1000 K, $\Delta G^\circ_{1000\ K}=15$ k. cal. If the pressure of Cl_2 is 1 atm, what will be the partial pressure of $PtCl_2$? [Ans. 8.7×10^{-4} atm.]

8.48. For the reaction

$$(CH_3)_2CHOH(g)=(CH_3)_2+CO(g)+H_2(g)$$

K_p at 457 K is 0.36, $\Delta C_p=4.0$, and $\Delta H^\circ_{298.2\ K}=14{,}700$ cal. (*a*) Derive an expression for $\log_{10} K_p$ as a function of T, and (*b*) calculate K_p at 500 K.

$$\left[(a)\ \textbf{Ans.}\ \log_{10}K_p=\frac{-2950}{T}+2.01\log_{10}T+0.656;\ (b)\ K_p=1.42.\right]$$

8.49. The equilibrium constant for the gas reaction $A=B$ is 0.10 at 27°C. Calculate (*a*) ΔG°, and (*b*) ΔG for the production of 1 mole of B at a pressure of 1 atm from A at a pressure of 20 atm. (*c*) Is the reaction spontaneous under the latter conditions?

[**Ans.** (*a*) +1373 cal. $mole^{-1}$, (*b*) −413 cal. $mole^{-1}$ (*c*) Yes.]

8.50. Mercuric oxide dissociates according to the reaction

$$2HgO(s)=2Hg(g)+O_2(g)$$

At 420°C the dissociation pressure is 387 torr, and at 450°C it is 810 torr. Calculate (*a*) the equilibrium constants, and (*b*) the enthalpy of dissociation per mole of HgO.

[**Ans.** (*a*) 0.0196, 0.1794 atm^3, (*b*) 36,750 cal. $mole^{-1}$.]

8.51. Calculate (*a*) K_p, and (*b*) ΔG° for the following reaction at 20°C

$$CuSO_4.4NH_3(s)=CuSO_4.2NH_3(s)+2NH_3(g)$$

The equilibrium pressure of NH_3 is 62 torr.

[**Ans.** (*a*) 6.66×10^{-3} atm^2, (*b*) 2920 cal.]

8.52. The following reaction takes place in the presence of aluminium chloride:

Cyclohexane(l)=Methylcyclopentane(l)

At 25° $K_c=0.143$, and at 45° $K_c=0.193$. From these data calculate (*a*) ΔG° at 25°, (*b*) ΔH°, and (*c*) ΔS°.

[**Ans.** (*a*) 1152 cal. $mole^{-1}$, (*b*) 2820 cal. $mole^{-1}$, (*c*) 5.59 cal. K^{-1} $mole^{-1}$.]

9

CHEMICAL KINETICS

Chemical kinetics concerns itself with the speed or rates of chemical reactions. In this area of chemistry we study the factors that control how fast chemical change occurs. These factors include:

(*a*) The nature of reactants and products.
(*b*) The concentration of reacting species.
(*c*) The effect of temperature.
(*d*) The effect of catalysts.

An understanding of the effect of these factors on the rates of reactions provides an insight into the mechanism of the reaction. The rate of a reaction tells us how fast the concentration of a reactant or product changes during the course of an investigation. The rate of a reaction can be expressed as the ratio of the change in the concentration of a reactant or product to a change in time. The rate, velocity or speed of a reaction is given by $+\frac{dc}{dt}$. This expression gives the increase (+) or decrease (—) of a concentration within a given time interval dt. Consider the reaction,

$$aA+bB+\ldots.=\text{Products} \qquad \ldots(1)$$

According to the law of mass action, the rate of a chemical reaction is proportional to the product of the molar concentration of the reactants, each raised to a power equal to the number of molecules of the substance undergoing reaction

$$\text{Rate} = -\frac{1}{a}\cdot\frac{dA}{dt}$$
$$= -\frac{1}{b}\cdot\frac{dB}{dt}\ldots. = k\,[A]^a\,[B]^b \qquad \ldots(2)$$

where k is the rate constant. The rate of decrease of each reacting component is given in terms of the number of mole equivalents of each species undergoing reaction.

The overall order n of a reaction is the sum of the exponents, i.e.,

$$n=a+b+\ldots. \qquad \ldots(3)$$

The reaction is of order a in reactant A, b in reactant B. Although it might appear that reactions of higher order are possible, it is doubtful whether n ever exceeds 3. The number of atoms or molecules taking part in each act leading to chemical reaction is called molecularity of the reaction.

First order reactions. In a first order reaction the rate is directly proportional to the concentration of one reactant

$$A \rightarrow \text{Products}$$

$$\frac{-d[A]}{dt} = k[A] \qquad \ldots (4)$$

where k is known as the rate constant or specific reaction rate. For a first order reaction k has the units of time^{-1}.

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right) \qquad \ldots (5)$$

where a is the initial concentration of reactant, $(a-x)$ is its concentration after time t. Hydrolysis of ethylacetate in presence of hydrochloric acid is a first order reaction. The acid acts as a catalyst

$$CH_3COOC_2H_5 + H_2O \overset{H^+}{\rightleftharpoons} CH_3COOH + C_2H_5OH$$

In order to follow the course of a reaction, a definite volume of the reacting solution, consisting of the ester dissolved in water containing the acid, is withdrawn and titrated with standard alkali. The volume of the alkali solution used is equivalent to the total of the hydrochloric acid and the acetic acid produced in the hydrolytic reaction

V_o =volume of alkali equivalent to the catalyst alone.

V_∞ =volume of alkali equivalent to the catalyst and the acetic acid formed by the hydrolysis of the whole of ester.

V_t =volume of alkali equivalent to the catalyst and the acetic acid formed by the hydrolysis of the ester in time t.

$V_\infty - V_o$ is equivalent to a

$V_\infty - V_t$ is equivalent to $a-x$

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_o}{V_\infty - V_t} \qquad \ldots (6)$$

Another reaction of the same type is the inversion of sucrose, i.e.,

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightleftharpoons \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

where α_o and α_∞ are the angles of rotation at the beginning and when the reaction is complete respectively and α_t is value after time t

$$k = \frac{2.303}{t} \log \frac{\alpha_o - \alpha_\infty}{\alpha_t - \alpha_\infty} \qquad \ldots (7)$$

Second order reactions. The rate of a second order reaction depends on two concentration terms; both these may refer to the same reactant or two different reactants.

(*a*) When two reactants are the same, the general reaction would be

$$2A \rightarrow \text{Products}$$

$$\frac{-dc}{dt} = k.\, C^2_{\text{A}} \qquad \ldots (8)$$

$$k = \frac{x}{t.a\,(a-x)}$$

where a is the initial concentration of reactant, $(a-x)$ is the concentration of the reactant after a time t and x is the amount of reactant reacted after time t.

(*b*) When two different reactants react,

$$A+B \rightarrow \text{Products}$$

$$\frac{dx}{dt} = k.\,(a-x)\,(b-x) \qquad \ldots (9)$$

$$k = \frac{2.303}{t\,(a-b)} \log \frac{b\,(a-x)}{a\,(b-x)} \qquad \ldots (10)$$

The units of specific reaction rate will be conc.$^{-1}$ time^{-1}.

Third order reactions. A third order reaction may involve three molecules of a single substance, two molecules of one substance and one of another, or all the three different molecules. Consider the reaction

$$3A \rightarrow \text{products}$$

$$\frac{dx}{dt} = k\,(a-x)^3 \qquad \ldots (11)$$

or

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] \qquad \ldots (12)$$

The units of specific reaction rate are conc.$^{-2}$ time^{-1}

Effect of temperature on reaction rate. Increase of temperature invariably enhances the rate of a chemical reaction to a marked extent. It can be expressed by means of an equation of the form

$$k = A.\, e^{-E_a/RT} \qquad \ldots (13)$$

where A is called the frequency factor and E_a is the energy of activation of the reaction. This equation is known as Arrhenius equation. On taking logarithms of equation (13), it is found that

$$\log k = \log A - \frac{E_a}{2.303\, RT}. \qquad \ldots (14)$$

A plot of log k vs $\frac{1}{T}$ gives a straight line and the slope gives the value of E_a.

Theories of reaction rate. In the collision theory a reaction takes place only if the molecules of the reactants collide. The rate (k) of such a reaction is given by

$$k = Zq \qquad \ldots (15)$$

where Z is the number of collisions per second per c.c. between like molecules of a gas, as for the reaction, $2HI \rightleftharpoons H_2 + I_2$ is given by,

$$Z_{11} = \tfrac{1}{2}\sqrt{2}\,\pi\,\sigma^2\,v\,(n')^2 \qquad \ldots (16)$$

where σ is the collision diameter of the molecules, v is the average velocity of the molecules, n' is the number of molecules per c.c.

Transition state theory. Consider a simple bimolecular reaction between the molecules of A and B

$$A + B \rightleftharpoons \underset{\text{Activated complex}}{[AB]^{\pm}} \rightarrow \text{Products.}$$

The specific reaction rate (k) is given by the relation

$$k = \frac{RT}{Nh} \cdot K^{\pm} \qquad \ldots (17)$$

where R is the gas constant, T is the absolute temperature, N is the Avogadro's number, h is Planck's constant and $K^{\pm}$ is the equilibrium constant, of the equilibrium, between the activated complex and the reactants.

Enzyme reactions. Enzyme reactions proceed in two stages:

(*a*) Formation of a complex between the enzyme and the substrate, as shown

$$E + S \underset{k'}{\overset{k}{\rightleftharpoons}} ES \qquad \ldots (18)$$

(*b*) Decomposition of the complex into reaction products, with regeneration of the enzyme

$$ES \xrightarrow{k_t} \text{Products} + E \qquad \ldots (19)$$

Let θ be the fraction of enzyme molecules that are involved in complex formation. The rate of formation will be proportional to the concentration of the free enzyme, i.e.,

$$(1-\theta)\,[E]_o$$

$[E]_o$ is the total enzyme, concentration, and also to the substrate concentration $[S]$.

$$v = k\,(1-\theta)\,[E]_o\,[S] \qquad \ldots (20)$$

The rate of reverse reaction v' is proportional to the concentration of the complex, θ

$$v' = k' \, \theta \, [E]_o$$

At equilibrium

$$k\,(1-\theta)\,[E]_o\,[S] = k'\,(\theta)\,[E]_o$$

$$\therefore \quad \frac{\theta}{1-\theta} = \frac{k}{k'}[S] \qquad \ldots (21)$$

Since $\frac{k}{k'} = K$, the equilibrium constant

$$\therefore \quad \theta = \frac{K\,[S]}{1+K[S]} \qquad \ldots (22)$$

Assuming that the reaction is proceeding extremely slowly, then the rate of reaction v_t will be proportional to the concentration of the complex

$$v_t = k_t \, \theta \, [E]_o \qquad \ldots (23)$$

On substituting the value of θ from Equation (22) in (23)

$$v_t = \frac{k_t \, K[S]\,[E]_o}{1+K\,[S]}$$

$$v_t = \frac{k_t\,[S]\,[E_o]}{K_m+[S]} \qquad \ldots (24)$$

where $K_m = \frac{1}{K}$ and known as Michaelis constant. It is also equal to the dissociation constant of the complex ES. On rearranging equation (24) we have,

$$\frac{v_t}{[S]} = \frac{k_t\,[E]_o}{K_m} - \frac{v_t}{K_m} \qquad \ldots (25)$$

Thus a plot of $\frac{v_t}{[S]}$ vs. v_t should give a straight line. The slope being $-\frac{1}{K_m}$. The intercept of this line on the v_t axis gives the maximum rate when the substrate concentration is so high that the enzyme is practically in the form of complex. This plot is known as Eadie plot.

Problem 9.1. The following data were obtained in an experiment on the inversion of cane-sugar:

Time (s)	0	432	1080	6120	∞
Angle of rotation (degrees)	+24.09	+21.40	+17.73	+15.00	−10.74

Show that the inversion of cane-sugar is a first order reaction.

Solution. Since the inversion of cane-sugar is a first order reaction,

$$k = \frac{2.303}{t} \log \frac{\alpha_o - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

where $\alpha_o = +24.09$

$$\alpha_\infty = -10.74$$

$$\alpha_o - \alpha_\infty = 24.09-(-10.74)$$

$$= +34.83$$

At $t=432$

$$k_1 = \frac{2.303}{432} \log \frac{34.83}{[21.40-(-10.74)]}$$

$$k_1 = \frac{2.303}{432} \log \frac{34.83}{32.14}$$

$$k_1 = 1.87 \times 10^{-4} \text{ sec}^{-1}.$$

At $t=1080$

$$k_1 = \frac{2.303}{1080} \log \frac{34.83}{[17.73-(-10.74)]}$$

$$k_1 = \frac{2.303}{1080} \log \left(\frac{34.83}{28.47}\right)$$

$$k_1 = 1.87 \times 10^{-4} \text{ sec}^{-1}.$$

At $t=1620$

$$k_1 = \frac{2.303}{1620} \log \frac{34.83}{[15.00-(-10.74)]}$$

$$k_1 = \frac{2.303}{1620} \log \frac{34.83}{25.74}$$

$$k_1 = 1.87 \times 10^{-4} \text{ sec}^{-1}.$$

Since the value of the rate constant k_1 is constant, it is a first order reaction.

Problem 9.2. A certain amount of methyl acetate was hydrolyzed in the presence of an excess of 0.05 mole dm^{-3} HCl at 25°C. When 25 ml aliquots of reaction mixture were removed and titrated with NaOH solution, the volume V of alkali required for neutralization after time were as follows:

t (min)	0	21	75	119	∞
V (ml)	24.4	25.8	29.3	31.7	47.2

Show that the reaction is the first order reaction.

Solution. $k = \frac{2.303}{t} \log \frac{V_\infty - V_o}{V_\infty - V_t}$

V_o = Volume of alkali required for the neutralization of HCl

V_∞ = Volume of alkali required for the neutralization of acid and complete hydrolysis of methyl acetate

$$V_\infty - V_o = 47.2 - 24.4 = 22.8$$

At $t=21$

$$k_1=\frac{2.303}{21}\log\frac{22.8}{21.4}$$

$$k_1=5.60\times10^{-5}\text{ sec}^{-1}.$$

At $t=75$

$$k_1=\frac{2.303}{75}\times\log\frac{22.8}{11.9}$$

$$k_1=5.60\times10^{-5}\text{ sec}^{-1}.$$

At $t=119$

$$k_1=\frac{2.303}{119}\log\frac{22.8}{15.5}$$

$$k_1=5.60\times10^{-5}\text{ sec}^{-1}.$$

Problem 9.3. For the reaction

$$A\rightarrow B+C$$

the following, were obtained:

Time of seconds	0	900	1800
Concentration of *A*	50.8	19.7	7.62

Find the order of the reaction.

Solution. For $t=900$ $a=50.8$

$$a-x=19.7$$

$$k_1=\frac{2.303}{900}\log\frac{50.8}{19.7}$$

$$k_1=1.05\times10^{-3}\text{ sec}^{-1}.$$

For $t=1800$

$$a=50.8$$

$$a-x=7.62$$

$$k_1=\frac{2.303}{1800}\log\frac{50.8}{7.63}$$

$$k_1=1.05\times10^{-3}\text{ sec}^{-1}.$$

The constant values of k show that the reaction is of first order.

Problem 9.4. From the following data, show that the decomposition of hydrogen peroxide in aqueous solution is a first order reaction.

Time (minutes)	0	5	10	20
$KMnO_4$ (ml)	46.1	37.1	29.8	19.6

Solution. For a first order reaction

$$k_1=\frac{2.303}{t}\log\frac{a}{a-x}$$

where $a=46.1$, the volume of $KMnO_4$ used at zero time and $(a-x)$

corresponds to the volume of $KMnO_4$ used at any time. Substituting the various values in the above equation:

$t=5$

$$k_1=\frac{2.303}{5}\ \log\frac{46.1}{37.1}$$

$$k_1=0.0435.$$

$t=10$

$$k_1=\frac{2.303}{10}\ \log\frac{46.1}{26.8}$$

$$k_1=0.0438.$$

$t=20$

$$k_1=\frac{2.303}{20}\ \log\frac{46.1}{19.6}$$

$$k_1=0.04290.$$

The values of k show that the reaction is of first order.

Problem 9.5. The reaction between nitric oxide and hydrogen proceeds according to the reaction,

$$2NO+2H_2 \rightleftharpoons N_2+2H_2O$$

The reaction has been investigated by measuring the initial rate of decrease of pressure in known mixtures of gases, when the following results were obtained at 700°C.

Initial pressure (atm)		Initial rate of decrease of pressure (atm min^{-1})
H_2	NO	
0.2	0.5	0.0048
0.1	0.5	0.0024
0.2	0.25	0.0012

Calculate (*a*) the order of the reaction with respect to each reactant and (*b*) the overall rate constant for the reaction at 700°C.

Solution. The initial rate of decrease of pressures is given by

$$\frac{-dp}{dt}=k.p_{NO}^{x}\,.\,p_{H_2}^{y} \qquad \ldots (1)$$

where p_{NO} and p_{H_2} are the initial pressure of NO and H_2 respectively, k is the rate constant and x and y are the orders with respect to NO and H_2.

Let v be the initial rate of decrease of pressure. The above equation can be written as,

$$v=k.p_{NO}^{x}.p_{H_2}^{y}$$

Taking logarithms of both sides of this equation

$$\log v = \text{constant} + x \log p_{NO} + y \log p_{H_2}$$

For the first and last set of data p_{H_2} is constant, so that

$$\log v = \text{constant} + x \log p_{NO}$$

$$\log \frac{v_1}{v_3} = x \log \frac{\left(p_{NO}\right)_1}{\left(p_{NO}\right)_3}$$

where v_1 and v_3 are the rates when the initial pressure of NO is $\left(p_{NO}\right)_1$ and $\left(p_{NO}\right)_3$ respectively.

On substituting the numerical values,

$$\log \left(\frac{0.0048}{0.0012}\right) = x \log \left(\frac{0.5}{0.25}\right)$$

$$x = 2.$$

The reaction is thus of order 2 with respect to NO.

Similarly for the first two sets of data, p_{NO} is constant, so that

$$\log v = \text{constant} + y \log p_{H_2}$$

$$\text{or} \quad \log \frac{v_1}{v_2} = y \log \frac{\left(p_{H_2}\right)_1}{\left(p_{H_2}\right)_2}$$

On substituting the numerical values

$$\log \left(\frac{0.0048}{0.0024}\right) = y \log \left(\frac{0.2}{0.1}\right)$$

$$\therefore \quad y = 1.$$

Thus the reaction is of order 1 with respect to H_2.

Hence the overall order $n = 2 + 1 = 3$. For a third order reaction the rate equation can be written as

$$\frac{-dp}{dt} = kp^2_{NO} \cdot p_{H_2}$$

$$\therefore \quad k = \frac{\dfrac{dp}{dt}}{p^2_{NO} \cdot p_{H_2}}$$

$$k = \frac{0.0048}{(0.5)^2\,(0.2)}$$

$$k = 0.096 \text{ atm}^{-2} \text{ min}^{-1}.$$

Problem 9.6. Decomposition of benzene diazonium chloride was studied at constant temperature by measuring the volume of N_2 evolved at various intervals of time and the following data were obtained:

Time (minutes)	0	20	50	70	∝
N_2 (ml)	0	10	25	33	162

From the above data show that the reaction is of first order.

Solution. The rate equation for the above reaction can be written as

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

where V_∞ and V_t are the volumes of nitrogen measured at the end of the reaction and at time t respectively. On substituting the various values in the above equation,

$$t=20,\ k_1 = \frac{2.303}{20} \log \frac{162}{162-10} = 0.00322$$

$$t=50,\ k_1 = \frac{2.303}{50} \log \frac{162}{162-25} = 0.00336$$

$$t=70,\ k_1 = \frac{2.303}{70} \log \frac{162}{162-35} = 0.00326.$$

Since the values of k are constant, the reaction is of first order.

Problem 9.7. The thermal dissociation of acetaldehyde was studied by Hinshelwood at 5.18° with the following results.

t(s)	42	73	105	190	242
$x=(P-P_i)$ (mm)	34	54	74	114	134

Show that the reaction is of second order. The initial pressure is 363 mm Hg.

Solution. The rate equation for a second order reaction is,

$$k = \frac{1}{t} \times \frac{x}{P_i(P_i - x)}$$

$$P_i = 363 \text{ mm Hg.}$$

The values can be calculated as under

(*i*) $t=42$ seconds

$$k = \frac{1}{t} \times \frac{x}{P_i(P_i - x)}$$

$$k = \frac{1}{42} \times \frac{34}{363 \times 329}$$

$$k = 6.79 \times 10^{-6}$$

(*ii*) $t=73$ seconds

$$k = \frac{1}{t} \times \frac{x}{P_i(P_i - x)}$$

$$k=\frac{1}{73}\times\frac{54}{363\times 309}$$

$$k=6.59\times 10^{-6}$$

(*iii*) $t=105$ seconds

$$k=\frac{1}{t}\times\frac{x}{P_i(P_i-x)}$$

$$k=\frac{1}{105}\times\frac{74}{363\times 291}$$

$$k=6.71\times 10^{-6}$$

(*iv*) $t=190$ seconds

$$k=\frac{1}{t}\times\frac{x}{P_i(P_i-x)}$$

$$k=\frac{1}{190}\times\frac{114}{363\times 249}$$

$$k=6.64\times 10^{-6}$$

(*v*) $t=242$ seconds

$$k=\frac{1}{t}\frac{x}{P_i(P_i-x)}$$

$$=\frac{1}{242}\times\frac{134}{363\times 229}$$

$$=6.66\times 10^{-6}.$$

Since the values of k comes out to be constant in each case it is a second order reaction.

Problem 9.8. In the thermal decomposition of N_2O at 764°C, the time required to decompose half the reactant was 263 seconds, when the initial pressure was 290 mm and 212 seconds at an initial pressure of 360 mm. What is the order of this reaction under the given conditions? Calculate the time required to decompose half the reactant when the initial pressure is one atmosphere.

Solution. For a reaction having time for half the reaction we have,

$$\frac{T_1}{T_2}=\left[\frac{a_2}{a_1}\right]^{n-1}$$

where T_1 is the half-change time when the initial concentration is a_1. T_2 is the half-change time when the initial concentration is a_2. n is order of reaction.

$$a_1=290 \text{ mm} \quad T_1=263 \text{ s}$$

$$a_2=360 \text{ mm} \quad T_2=212 \text{ s}$$

$$\frac{263}{212}=\left[\frac{360}{290}\right]^{n-1}$$

$$1.24=(1.24)^{n-1}$$
$$n-1=1$$
$$n=2$$

Hence the reaction is of second order.

We know that for a second order reaction the product of half-reaction time and initial concentration is constant.

$$\therefore \quad 263\times 290 \text{ mm}=7.63\times 10^{4}$$

We are given that the initial pressure is 760 mm and let T be the time in second for half-reaction.

$$\therefore \quad 760\times T=7.63\times 10^{4}$$
$$T=100.2 \text{ seconds.}$$

Problem 9.9. The following values for the first order rate constant were obtained for a certain reaction:

Temp (°C)	$k\times 10^{-5}\ \text{s}^{-1}$
25	3.46
35	13.50

Calculate the Arrhenius frequency factor.

Solution. Arrhenius equation can be written as

$$\log \frac{k_2}{k_1}=\frac{E_a}{2.303\ R}\left(\frac{T_2-T_1}{T_1\ .\ T_2}\right)$$

where

$$k_1=3.46\times 10^{-5}\ \text{s}^{-1}$$
$$k_2=1.35\times 10^{-4}\ \text{s}^{-1}$$
$$T_1=298\text{K.} \qquad T_2=308\text{K}$$

On substituting these values in the above equation we get

$$\log \frac{1.35\times 10^{-4}}{3.46\times 10^{-5}}=\frac{E_a}{2.303\times 1.987}\left(\frac{308-298}{298\times 308}\right)$$

$$\therefore \quad E_a=\frac{2.303\times 1.987\times 298\times 308}{10}\ \log \frac{1.35\times 10^{-4}}{3.46\times 10^{-5}}$$
$$=24830 \text{ calories.}$$

Since Arrhenius equation has the form

$$\log\ k_1=\frac{-E_a}{2.303\ RT}+\log A$$

$$\log 3.46\times 10^{-5}=\frac{24830}{2.303\times 1.987\times 298}+\log A$$

$$\log A\ =13.7491$$
$$A\ =5.611\times 10^{13}.$$

Problem 9.10. The concentration of tert-butyl bromide as a function of time for the reaction

$$(CH_3)_3\ CBr+H_2O\rightarrow(CH_3)_3\ COH+HBr$$

at 25°C is given in the table below.

Time (*hr.*)	*Conc. of* $(CH_3)_3\ CBr$ (*mole/l*)
0	0.1039
3.15	0.0896
4.10	0.0859
6.20	0.0776
8.20	0.0701
10.0	0.0639
13.5	0.0529

What is the order of $(CH_3)_3\ CBr$ in the rate expression? (H_2O is a solvent. Its concentration remains approximately the same).

Solution. Select any two intervals and determine the rate.

rate (mole/l-hr)	average conc. (mole/l)
$\frac{0.0896-0.1039}{3.15}$	0.0967
$\frac{0.0859-0.0896}{4.10-3.15}$	0.0878

$$\text{rate} = -k[(CH_3)_3CBr]^{n_A}\,[H_2O]^{n_B}$$

$$\frac{\frac{-0.0143}{3.15} = k\ (0.0967)^{n_A}[H_2O]^{n_B}}{\frac{-0.0037}{0.95} = k\ (0.0878)^{n_A}[H_2O]^{n_B}}$$

$$\frac{0.00454}{0.00390} = \frac{(0.0967)^{n_A}}{(0.0878)^{n_A}}$$

$$1.16 = 1.10^{n_A} \qquad n_A = 1$$

Therefore, $(CH_3)_3$ CBr is first order.

Problem 9.11. For the chemical reaction $A+B \rightarrow C$ the following rate data were found.

Initial rate (*mole/l−sec*)	*Initial conc.* *A* (*mole/l*)	*Initial conc.* *B* (*mole/l*)
0.10	2.0	3.0
0.90	6.0	3.0
0.90	6.0	6.0

Find the rate expression from these data.

Solution. $\text{Rate} = k\ [A]^{n_A}\ \ [B]^{n_B}$

$$\frac{0.90 = k\ (6.0)^{n_A}(3.0)^{n_B}}{0.10 = k\ (2.0)^{n_A}\ (3.0)^{n_B}}$$

$$9=3^{n_A} \qquad n_A=2$$

$$\frac{0.90}{0.90}=\frac{k\,(6.0)^2\,(6.0)^{n_B}}{k\,(6.0)^2\,(3.0)^{n_B}}$$

$$1=2^{n_B} \qquad n_B=0 \;\; [B]^\circ=1$$

Therefore, rate $=k\,[A]^2$

Problem 9.12. The following data were observed for the reaction

$$I^-+OCl^-=Cl^-+OI^-$$

carried out in a basic solution (OH^- Present)

Initial rate (mole/l—sec) (disappearance of OCl^-)	*Initial concentrations* $[I^-]$ *(mole/l)*	$[OCl^-]$ *(mole/l)*	$[OH^-]$ *(mole/l)*
1.75×10^{-4}	0.002	0.002	1.00
8.75×10^{-5}	0.001	0.002	1.00
4.37×10^{-5}	0.001	0.001	1.00
8.75×10^{-5}	0.001	0.001	0.50

What is the rate expression, the order of the reaction, and the rate constant?

Solution. rate $=-k\,[I^-]\,[OCl^-]\,[OH^-]$

let $I^-=A$, $OCl^-=B$, $OH^-=C$.

$$\frac{-1.75\times10^{-4}}{-8.75\times10^{-5}}=\frac{-k\,(0.002)^{n_A}\,(0.002)^{n_B}\,(1.00)^{n_C}}{-k\,(0.001)^{n_A}\,(0.002)^{n_B}\,(1.00)^{n_C}}$$

$$2=2^{n_A} \qquad n_A=n_I=1$$

$$\frac{-8.75\times10^{-5}}{-4.37\times10^{-5}}=\frac{-k\,(0.001)\,(0.002)^{n_B}\,(1.00)^{n_C}}{-k\,(0.001)\,(0.001)^{n_B}\,(1.00)^{n_C}}$$

$$2=2^{n_B} \qquad n_B=n_{OCl^-}=1$$

$$\frac{-4.37\times10^{-5}}{-8.75\times10^{-5}}=\frac{-k\,(0.001)\,(0.001)\,(1.00)^{n_C}}{-k\,(0.001)\,(0.001)\,(0.50)^{n_C}}$$

$$\tfrac{1}{2}=2^{n_C} \qquad n_C=n_{OH^-}=-1$$

$$\text{rate}=\frac{k\,[I^-]\,[OCl^-]}{[OH^-]}$$

order of reaction $=1+1-1=1$

$$\frac{4.37\times10^{-5}\text{ mole}}{\text{l—sec}}=-k\,\frac{(0.001)^2\text{ mole}^2/\text{l}^2}{1.00\text{ mole/l}}$$

$$k=4.37\times10\text{ s}^{-1}$$

Problem 9.13. For the chemical reaction

$$5\,Br^-+BrO_3^-+6H^+\rightarrow3Br_2+3H_2O$$

the rate expression is given as

$$\text{rate}=k\,[Br^-]\,[BrO_3^-]\,[H^+]^2$$

What is the molecularity and order of each reactant?

Solution.

Reactant	*Order*	*Molecularity*
Br^-	1	5
BrO_3^-	1	1
H^+	2	6

Problem 9.14. In the study of the chemical reaction

$$2FeCl_3+SnCl_2 \rightarrow SnCl_4+2FeCl_3$$

in which equal concentrations of ferric chloride and stannous chloride were used. The following data were obtained:

t (minutes)	0	2	5	10	25
Concentration of $FeCl_3$ (moles per litre)	0.0700	0.0423	0.0304	0.0225	0.0147

Show that the reaction is a third order reaction.

Solution. For a third order reaction of this type the rate constan k_3 is given by

$$k_3=\frac{1}{2t}\left[\frac{1}{(a-x)^2}-\frac{1}{a^2}\right]$$

$$k_3=\frac{x}{2t}\,\frac{(2a-x)}{a^2(a-x)^2}$$

when $t=0$, $x=0$ $a-x=a$ $a=0.0700$

$t=2$

$$a-x=0.0423 \text{ mole/l}$$

$$x=0.0277$$

$$2a-x=0.1400-0.0277=0.1123$$

$$k_3=\frac{1}{2\times 2}\times\frac{(0.1123)(0.0277)}{(0.07)^2\,(0.0423)^2}$$

$$k_3=88.7$$

$t=5$

$$a-x=0.0304$$

$$x=0.0700-0.0304$$

$$=0.0396$$

$$2a-x=0.1400-0.0396$$

$$=0.1004$$

$$k_3 = \frac{1}{2\times 10} \times \frac{(0.1004)(0.0396)}{(0.07)^2\ (0.0304)^2}$$

$$= 87.8$$

$t=10$

$$a-x=0.0225$$

$$x=0.0700-0.0225$$

$$=0.0475$$

$$2a-x=0.1400-0.0553$$

$$=0.0847$$

$$k_3 = \frac{1}{2\times 10} \times \frac{(0.0925)(0.0475)}{(0.07)^2\ (0.0225)^2}$$

$$=88.6$$

$t=25$

$$a-x=0.0147$$

$$x=0.0700-0.0147$$

$$=0.0553$$

$$2a-x=0.0847$$

$$k_3 = \frac{1}{2\times 25} \times \frac{(0.0847)(0.553)}{(0.07)^2\ (0.0147)^2}$$

$$=88.4$$

Problem 9.15. The chemical reaction between mercuric chloride and potassium oxalate proceeds as under:

$$2HgCl_2 + K_2C_2O_4 \rightarrow KCl + 2CO_2 + Hg_2Cl_2$$

The weight of Hg_2Cl_2 precipitated from different solutions in a given time, at 100°C was as follows:

	$HgCl_2$ moles per litre	*$K_2C_2O_4$ moles per litre*	*Time minutes*	*Hg_2Cl_2 precipitated moles*
(*i*)	0.0836	0.404	65	0.0068
(*ii*)	0.0836	0.202	120	0.0031
(*iii*)	0.0418	0.404	66	0.0032

From these data, calculate the order of the reaction.

Solution. The rate equation for the chemical reaction may be written as

$$\frac{dx}{dt} = k[HgCl_2]^{n_1}\quad [K_2C_2O_4]^{n_2}$$

$$\frac{0.0068 \text{ mol}}{65 \text{ min}}=k[\text{HgCl}_2]^{n_1}[\text{K}_2\text{C}_2\text{O}_4]^{n_2}$$

$$=k[0.0836 \text{ mol l}^{-1}]^{n_1}[0.404 \text{ mol l}^{-1}]^{n_2}$$

$$\frac{\Delta x_2}{\Delta t_2}=k[0.0836 \text{ mol l}^{-1}]^{n_1}[0.202 \text{ mol l}^{-1}]^{n_2}$$

$$\frac{0.0031}{120 \text{ min}}=k[0.836 \text{ mol l}^{-1}]^{n_1}[0.202 \text{ mol l}^{-1}]^{n_2}$$

$$\frac{\Delta x_1}{\Delta t_1}\bigg/\frac{\Delta x_2}{\Delta t_2}=\frac{k[0.0836 \text{ mol l}^{-1}]^{n_1}[0.404 \text{ mol l}^{-1}]^{n_2}}{k[0.0836 \text{ mol l}^{-1}]^{n_1}[0.202 \text{ mol l}^{-1}]^{n_2}}$$

$$4.05\simeq 2^2=2^{n_2}$$

$$\therefore \quad n_2=2$$

For $\Delta x_3=0.0032$ mole $\quad t_3=60$ min

$$\frac{\Delta x_1}{\Delta t_1}\bigg/\frac{\Delta x_3}{\Delta t_3}=\frac{k[0.0836 \text{ mol l}^{-1}]^{n_1}[0.404 \text{ mol l}^{-1}]^{n_2}}{k[0.0418 \text{ mol l}^{-1}]^{n_1}[0.404 \text{ mol l}^{-1}]^{n_2}}$$

$$\frac{0.0068 \text{ mole}}{65 \text{ min}}\bigg/\frac{0.032 \text{ mole}}{60 \text{ min}}=2^{n_1}$$

$$1.96\simeq 2=2^{n_1}; \qquad n_2=1$$

$\therefore$ Order of reaction$=n_1+n_2=2+1=3.$

Problem 9.16. For the chemical reaction

$$A+B+C\rightarrow E$$

it was found that the rate of the reaction doubled when the concentration of B was doubled, that the rate double when the concentrations of both A and B were doubled and quadrupled when the concentrations of both B and C were doubled. What is the rate expression, the order of each component, and the order of the reaction?

Solution. For the above reaction,

$$\text{rate}=k[A]^{n_A}[B]^{n_B}[C]^{n_C}$$

For the conditions given we can write the following expressions:

$$\frac{2}{1}=\frac{k[A]^{n_A}(2)^{n_B}[C]^{n_C}}{k[A]^{n_A}(1)^{n_B}[C]^{n_C}}$$

$$2=(2)^{n_B}$$

$$n_B=1$$

$$\frac{2}{1}=\frac{k(2)^{n_A}(2)^1[C]^{n_C}}{k(1)^{n_A}(1)^1[C]^{n_C}}$$

$$2=(2)^{n_A}(2)$$

$$1 = 2^{n_A}; \qquad n_A = 0$$

$$\frac{4}{1} = \frac{k[A]^{n_A}\,(2)^1\,(2)^{n_C}}{k[A]^{n_A}(1)^1\,(1)^{n_C}}$$

$$4 = (2)\,(2)^{n_C}\ ; \quad n_C = 1$$

$\therefore$ $\quad$ rate $= k[B]\,[C]$

reaction order $= 0 + 1 + 1 = 2$.

Problem 9.17. The mechanism for the overall reaction is

$$A_2 + B \rightarrow D$$

$A_2 \rightarrow 2A$	slow
$2A + B \rightarrow C$	fast

If a catalyst D changes the mechanism to

$A_2 + D \rightarrow A_2D$	slow
$A_2D \rightarrow 2A + D$	fast
$2A + B \rightarrow C$	

What is the rate expression for the reaction with and without a catalyst?

Solution. Without the catalyst; the slow step is the

$$A_2 \rightarrow 2A$$

rate determining step. Therefore, rate of the reaction,

$$\text{rate} = k[A_2]$$

with the catalyst, the slow step is

$$A_2 + D \rightarrow A_2D$$

$\therefore$ $\quad$ rate $= k'[A_2][D]$.

Problem 9.18. The following values have been obtained for the velocity constant in the decomposition of N_2O_5:

t (°C)	0	25	45	65
k (mm^{-1})	4.7×10^{-5}	2.0×10^{-3}	3.0×10^{-2}	3.0×10^{-1}

Find the value of activation energy and Arrhenius factor from these data.

Solution. The Arrhenius equation in the logarithmic form is,

$$\log k = \log A - \frac{E}{2.303\,RT}$$

where E is the energy of activation, R is gas constant, T is the temperature in K and A is called the frequency factor or pre-exponential factor. The plot of $\log k$ vs $\frac{1}{T}$ should give a straight line.

T (K)	273	298	318	338
$1/T$	3.66×10^{-3}	3.36×10^{-3}	3.15×10^{-3}	2.96×10^{-3}
$\log k$	−4.328	−2.699	−1.523	−0.523

A plot of $\log k$ vs $1/T$ is shown in Fig. 9.1.

From the Arrhenius equation slope is

$$\frac{-E}{2.323\,R}=\frac{3.23}{0.6\times10^{-3}}.$$

$$E=103\text{ kJ mole}^{-1}$$

At 0°C

$$-4.328=\log A-\frac{103{,}000}{2.303\times8.31\times273}$$

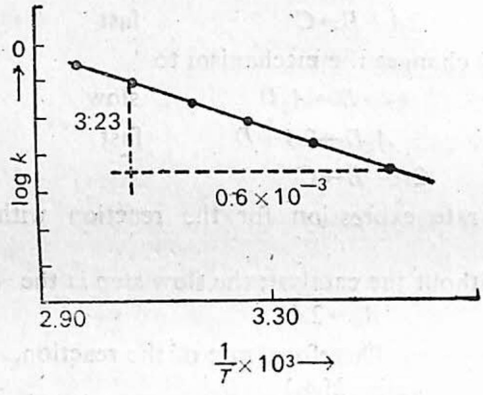


Fig. 9.1.

$$\log A=\frac{103{,}000}{2.303\times8.31\times273}-4.328$$

$$\log A=15.382$$

$$A=2.41\times10^{15}\text{ min}^{-1}.$$

Problem 9.19. At 283°C at a concentration of one mole per litre, the number of molecules of hydrogen iodide colliding per second is 6.0×10^{31} per ml. The activation energy of the reaction is 187 kJ. Calculate the number of molecules reacting per ml.

Solution. Let Z be the number of molecules colliding per ml per second in a system containing one mole of reactant per litre. The fraction (x) of these molecules is activated as a result of collision, then the reaction rate constant (k) for the bimolecular reaction is given by

$$k=Zx$$

Further x is given by

$$x=e-E/RT$$

$$k=Ze-E/RT$$

$$k=6\times 10^{31}\ e-187000/(8.31\times 556)$$

Taking logarithms of both sides we get,

$$\log k=\log(6\times 10^{31})-\frac{187000}{8.31\times 2.303\times 556}$$

$$\log k=31.778-17.57$$

$$\log k=14.208$$

$$k=1.614\times 10^{14}\text{ molecules reacting ml}^{-1}\text{ s}^{-1}$$

The number of molecules reacting is 1.6×10^{14} ml^{-1} s^{-1}.

Problem 9.20. Calculate the number of collisions per second per cubic centimetre at 0°C in a hydrogen gas at a pressure of 1.0 atm. The value of van der Waals constant, $b=0.026$ c.c.

Solution. Number of molecules per cubic centimetre, n'

$$n'=Nn=\frac{NPV}{RT}$$

$$n'=\frac{(6.02\times 10^{23}\text{ molecules})(1.00\text{ atm})0.00100\text{ litre}}{0.082\text{ litre atm deg}^{-1}\text{ mole}^{-1}\times 273}$$

$$n'=2.68\times 10^{19}\text{ molecules.}$$

σ for hydrogen can be calculated from the van der Waals constant, b

$$V_m=b/4=0.0266\times 10^{3/4}=6.65\text{ cm}^3\text{ mole}^{-1}.$$

$$\text{Volume per mole }=\frac{V_m}{N}=\frac{6.65\text{ cm}^3\text{ mole}^{-1}}{6.02\times 10^{23}\text{ molecules mole}^{-1}}$$

$$=1.10\times 10^{-23}\text{ cm}^3/\text{molecule.}$$

Since $V=4/3\ \pi r^3$ for any sphere and the radius of the molecule is $\sigma/2$,

$$V=\pi/6\ \sigma^3$$

$$\sigma=\sqrt{\frac{6(1.10\times 10^{-23})\text{ cm}^3}{3.14}}$$

$$\sigma=2.76\times 10^{-8}\text{ cm}$$

The number of collisions per second per cubic centimetre in any gas

$$Z=2(n')^2\ \sigma^2\sqrt{\frac{\pi RT}{M}}\ .$$

$$Z=2\ (2.68\times 10^{19})^2.(2.76\times 10^{-8})^2\sqrt{\frac{3.14\ (8.314\times 10^{7})\ 273}{2.01}}$$

$$Z=2.06\times 10^{29}\text{ collisions/sec.}$$

EXERCISES

9.1. The mechanisms of three reactions are given below. In each case write down the form of the rate equation and give the order with respect to each reactant.

(*a*) $A+B \rightarrow C$
$A+B \rightarrow C$ single bimolecular
(*b*) $P+Q \rightarrow R$
$R \rightleftharpoons S$ slow
$S+Q \rightleftharpoons R$ fast
(*e*) $L+2M \rightarrow N$
$2M \rightarrow M_2$ fast
$M_2+L \rightarrow N$ slow.

[**Ans.** (*a*) $k_2\,[A]\,[B]$, first and first
(*b*) $k_1\,[P]$, first and zero
(*c*) $k_3\,[M]^2\,[L]$, second and first.]

9.2. The muta-rotation of glucose is a proton-catalysed reaction. The following polarimeter readings were observed for the reaction at 25°C. When the concentration of hydrochloric acid in the reaction mixture was 0.01 mole litre^{-1}.

Time (s)	0	300	1500	∞
Polarimeter readings	33.2	31.2	25.5	18.6

Calculate the first order velocity constant under these conditions.

[**Ans.** 4.71×10^{-4} s^{-1}.]

9.3. The kinetics of the alcoholysis of cinnamal chloride was studied spectroscopically and the following results for the absorbance as a function of time were obtained.

Absorbance	0.378	0.339	0.295	0.246	0.204
Time (min)	0	20	40	70	100
Absorbance	0.178	0.148	0.107	0.006	
Time (min)	120	150	200	∞	

Calculate the rate constant for the reaction. [**Ans.** 1.07×10^{-4} s^{-1}.]

9.4. The acid catalysed hydrolysis of acetal at 35°C proceeds in the presence of excess of water and is a first order process.

$$CH_3CH(OC_2H_5)_2+H_2O \rightarrow CH_3CHO+2C_2H_5OH$$

The change in volume during the reaction was measured with a dilatometer and the following results were obtained.

Dilatometer reading/cm	0	97	113	147	159	171	179	184	187
Time (min)	0	3	5	8	10	12	15	20	∞

Calculate the rate constant and the half life of the reaction.

[**Ans.** $k=3.45\times10^{-3}$ s^{-1}; $t_{1/2}=200$ s.]

9.5. The rate of disintegration of a radioactive sample gave the following results:

Days	1	3	5	7	9
Rates	6200	4700	—	2800	2100

Show that the data obey a first order rate law. Find the half-life and evaluate the rate at t=5. [Ans. $t_{1/2}$=5.4 days.]

9.6. The rate constant for the decomposition of hydrogen iodide is 3.96×10^{-6}l mole^{-1} s^{-1} at 321.4°C, and a=1 m. l^{-1}. Calculate (*i*) the extent of decomposition after 20 hrs., and (*ii*) the half-life.

[Ans. (*i*) 22 per cent, (*ii*) 2.5×10^{5} s.]

9.7. A solution of N_2O_5 in CCl_4 at 45°C produces 5.02 c.c. of O_2 in 1198 s, 7.33 c.c. of O_2 in 2315 s and a maximum of 9.58 c.c. of O_2 after a longtime. Show that these results conform to a first-order rate law, for decomposition of N_2O_5 and find the first-order rate constant.

[Ans. $k=6.2\times10^{-4}$ s^{-1}]

9.8. A solution containing equal concentrations of ethylacetate and sodium hydroxide is 25 per cent saponified in 5 min. Show that for this system 50 per cent saponification will be reached in 15 min. What will be the percentage of saponification in 10 min.? [Ans. 40 per cent.]

9.9. For the gas phase reaction $2NO+2H_2\rightarrow N_2+2H_2O$ the following initial rates were measured at 826°C.

$(P_{H_2})_0$ =400 torr				*$(P_{NO})_0$ =400 torr*			
$(P_{NO})_0$ (torr)	359	300	152	$(P_{H_2})_0$ torr	289	205	147
$-\left(\frac{dP}{dt}\right)_0$ (torr s^{-1})	1.50	1.03	0.25		1.60	1.10	0.79

Determine the order of reaction with respect to each reactant.

[Ans. $n_{NO}=2$ $n_{H_2}=1$.]

9.10. Two substances A and B undergo a bimolecular reaction step. The following table gives the concentration of A at various times for an experiment carried out at a constant temperature of 17°C.

Concentration of $A\times10^4$ mole/dm^{-3}	10.00	7.94	6.31	5.01	3.98
Time (min)	0.00	10.00	20	30	40

The initial concentration of B is 2.5 mole dm^{-3}. Calculate the value of the second order rate constant. [Ans. 1.54×10^{-4} dm^3 mole^{-1} s^{-1}.]

9.11. The process of breathing maintains the concentration of oxygen in the human blood in the lungs at 1.6×10^{-6} moles of oxygen per litre of blood. The oxygen in the blood reacts with a compound, haemoglobin (Hb) to yield oxyhaemoglobin (HbO_2).

$$Hb+O_2\rightarrow HbO_2$$

The lung processes keep the concentration of haemoglobin constant in the lungs at 1.6×10^{-6} moles of oxygen per litre of the blood. The velocity constant for the reaction is $k=2.1\times10^{-6}$ litre mole^{-1} s^{-1} at body temperature. Calculate (*a*) the rate of formation of oxyhaemoglobin per litre of blood, and (*b*) the rate of consumption of oxygen per litre of blood.

[Ans. (*a*) 2.7×10^{-5} mole litre^{-1} s^{-1}, (*b*) 2.7×10^{-5} mole litre^{-1} s^{-1}].

9.12. A solution was found to have the following concentrations at the times stated after making up:

Time (s)	0	600	3000	6000	9000
Concentration (mole/litre^{-1})	1.000	0.9616	0.8235	0.6776	0 5572

Find the order of the reaction and the time required for 50 per cent decomposition. [Ans. First order, $k_1=6.49\times10^{-5}$ s^{-1}; $t_{1/2}=1.07\times10^{4}$ s.]

9.13. Suggest a rate law for the reaction

$$2NO(g)+Cl_2(g)\rightarrow 2NOCl(g)$$

Exp. No.	C_{NO} (*M*)	C_{Cl_2} (*M*)	*Relative initial rates*
1.	0.10	0.10	1
2.	0.20	0.20	8
3.	0.10	0.20	2

$\left[\text{Ans.} \quad \frac{-dC_{NO}}{dt}=kC^2_{NO}\times C_{Cl_2}.\right]$

9.14. Suggest a rate law for the reaction

$$2N_2O_5(g)\rightarrow 2N_2O_4(g)+O_2(g)$$

Exp No.	*initial* $C_{N_2O_5}$ (*mole litre*$^{-1}$)	*Relative initial rates*
1.	0.10	1.0
2.	0.050	0.50
3.	0.25	2.50

[Ans. Rate $=k\times C_{N_2O_5}$.]

9.15. Suggest a rate law for the following reaction

$$2NO(g)+2H_2(g)\rightarrow N_2(g)+2H_2O(g)$$

Exp. No.	*Initial* C_{NO}	*Initial* C_{H_2}	*Relative initial rates*
1.	0.1	0.1	1.0
2.	0.1	0.01	0.1
3.	0.01	0.1	0.01

[Ans. Rate $=kC^2_{NO}\times C^2_{H_2}$.]

9.16. The catalysed decomposition of H_2O_2 in aqueous solution is followed by removing equal volumes of samples at various time intervals and titrating them with $KMnO_4$ to determine undecomposed H_2O_2. The results obtained are:

Time (minutes)	5	10	20	30	50
ml of $KMnO_4$	37.1	29.8	19.6	12.3	5.0

Show graphically that the reaction is first order. From the graph calculate the value of the rate constant. [Ans. 0.0437 min^{-1}.]

9.17. At 100°C the gaseous reaction $A\rightarrow 2B+C$ is observed to be first order. On starting with pure *A* it is found that at the end of 10 minutes the total pressure of the system is 176.0 mm Hg and after a long time is 270.0 mm. Calculate the half-life period of the reaction. [Ans. 10.7 min.]

9.18. Show that the half-life equation for the second order process is

$$dn/dt=k_2(A)^2 \text{ is } t_{1/2}=1/(k_2a)$$

9.19. Some phosphine gas PH_3(g) is introduced into a flask at 600°C containing inert gas. The PH_3 proceeds to decompose into P_4(g) and H_2(g) and the reaction goes to completion. The total pressure as a function of time changes as under:

Time (sec)	0	60	120	∞
P_4 (mm Hg)	262.40	272.90	275.53	286.40

(*i*) Calculate the order of reaction and the specific rate constant.

(*ii*) The back reaction obeys a rate law of the form:

$$\frac{dP_{NH_3}}{dt}=k_2 P^a_{P_4} . P^b_{H_2}$$

Calculate the values of *a* and *b*.

[**Ans.** (*i*) The reaction is a first order reaction $k_1=0.023$ sec^{-1} (*ii*) $a=1/4$, $b=3/2$.]

9.20. A certain first order reaction is found to have a rate constant $k_1=0.0430$ s^{-1} at 75°C and an activation energy $E_a=98.2$ kJ mole^{-1}. Calculate $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the reaction at 75°C.

[**Ans.** $\Delta H^{\neq}=95.3$ kJ; $\Delta S^{\neq}=1.34$ kJ K^{-1}.]

9.21. The inversion of sucrose proceeds with a constant half-life of 500 min at a constant pH of 5 at 25°C. At this temperature, but at pH of 4, the half-life is a constant at 50 min. The rate law obeys the rate equation

$$\frac{d\,(\text{sucrose})}{dt}=-k\,(\text{sucrose})^a\,(\text{H}^+)^b$$

Explain what the exponents *a* and *b* should be.

[**Ans.** A constant half-life means that the reaction is first order, hence $a=1$. Since a ten-fold increase in [H$^+$] decreases the half-life and hence increase the rate ten-fold, *b* must also be one.]

9.22. The reaction $C_3H_7Br+S_2O_3^{2-}=C_3H_7S_2O_3^-+Br^-$ is bimolecular and the second order specific rate constant is 1.64×10^{-3} sec^{-1} M^{-1} at 37°C. The initial concentrations in a particular experiment are: $[A]=0.1$ M and $[S_2O_3]=0.1$ M where *A* denotes the C_3H_7Br concentration. (*i*) Calculate the initial rate $\frac{dA}{dt}$. (*ii*) Derive the integrated rate law for this experiment.

[**Ans.** (*i*) $\frac{dA}{dt}=-k\,[A]\,[S_2O_3]^2$, (*ii*) $\frac{1}{A}-\frac{1}{\mathring{A}}=kt.$]

9.23. The rate of saponification of methyl acetate at 25°C was studied by making up a solution 0.01 molar in both base and ester, and titrating the mixture at various times with standard acid. The following data were obtained:

Time (min)	3	5	7	10	15	21	25
Concentration of base found	0.00740	0.00634	0.00550	0.00464	0.00636	0.00288	00.0254

Show by a graphical method that the reaction is a second order, and determine the specific rate constant. [**Ans.** 11.7 litre mole^{-1} min^{-1}.]

9.24. For the reduction $2FeCl_3+SnCl_2\rightarrow2FeCl_2+SnCl_4$ in aqueous solution the following data were obtained at 25°C.

t (min)	1	3	7	11	40
y	0.01434	0.02664	0.03612	0.04102	0,05058

where *y* is the amount of $FeCl_3$ reacted in moles per litre. The initial concentrations of $SnCl_4$ and $FeCl_3$ were 0.03125 and 0.0625 mole/litre respectively. Show that the reaction is third order, and calculate the average specific rate constant. [**Ans.** 80 mole^{-2} litre^2 min^{-1}.]

9.25. The racemization of pinene is a first order reaction. In the phase the specific rate constant was found to be 2.2×10^{-5} min^{-1} at 457.6 K and 3.07×10^{-3} at 510.1 K. Estimate the energy of activation from these data at 480 K. [**Ans.** $E_a = 43{,}600$ cal. mole^{-1}.]

9.26. The gas phase reaction $2A \rightarrow B + C$ is bimolecular with an activation energy of 24,000 cal./mole. The molecular weight and diametre of A are 60 and 3.5. Å respectively. Calculate the specific rate constant for the decomposition at 27°C. [**Ans.** $3.8 \times 1S^{-7}$ litre mole^{-1} sec^{-1}.]

9.27. (*a*) Integrate the rate equation

$$-dc/dt = kC^{\frac{1}{2}}$$

(*b*) Derive an expression for $t_{\frac{1}{2}}$ in terms of k and C_0

(*c*) What are the units of k.

[**Ans.** (*a*) $2\,(C_0^{\frac{1}{2}} - C^{\frac{1}{2}}) = kt$

(*b*) $t_{\frac{1}{2}} = \dfrac{2.586 C_0^{\frac{1}{2}}}{k}$

(*c*) mole$^{-\frac{1}{2}}$ dm$^{-\frac{3}{2}}$ s^{-1}.]

9.28. The reaction between ozone and CS_2 was studied at 29.3°C with excess CS_2 to find the order of reaction with respect to O_3. From the following data prove that the reaction is second order and determine the pseudo-second order rate constant.

t (min)	0.0	0.5	1.0	2.0	3.0	4.0
P_{O_3} torr	1.76	1.04	0.79	0.92	0.37	0.29

[**Ans.** Since the plot of $1/P_{O_3}$ against t is linear it is a second order reaction, $k = 1.20 \times 10^{-2}$ torr^{-1} s^{-1}.]

9.29. A rule often quoted in the laboratory is "heat the sample by 10°C and the reaction will proceed twice as fast." This is true at any given temperature only for reactions having one value of ΔE. Find the value of ΔE if $t_1 = 25$°C and $t_2 = 35$°C. [**Ans.** 52.9 kJ mole^{-1}.]

9.30. A drug is given intravenously and blood concentrations measured at 1 and 4 hours are 26 and 18μ g/ml, what is the half-life and at what time will the levels decrease to 10μ g/ml? [**Ans.** $t_{\frac{1}{2}} = 5.7$ hours; 8.8 hours.]

9.31. Sulphadiazine has a half-life of 17 hours. If it is to be given as single daily dose of 1000 mg, and is rapidly absorbed, what initial dose should be used to obtain plateau serum levels at the end of the first 24 hours.

[**Ans.** 1600 mg.]

9.32. The first order decomposition of N_2O_5 to give NO_2 and O_2 has a specific rate constant of 4.30×10^{-5} sec^{-1} at 300 K and 6.97×10^{-2} sec^{-1} at 500 K. Calculate the activation energy for this reaction. [**Ans.** 24.8 k. cal.]

9.33. A reaction has an activation energy for 25 k. cal. and a specific constant $k = 5.0 \times 10^{-2}$ sec^{-1} at 400 K. Find the specific rate constant at 500 K.

[**Ans.** 27 sec^{-1}.]

9.34. Calculate the relative velocity and kinetic energy as well as the centre-of-mass velocity and kinetic energy for

(*a*) K and Cl_2 are moving on paths that intersect at right angles with velocities 5.0×10^2 and 3.0×10^2 ms^{-1}, re pectively.

(*b*) H_2 and Cl_2 moving as in (*a*).

(*c*) K and Cl_2 moving on paths that intersect at 60° with the same velocities as in (*a*).

[Ans. (*a*) Relative $v=5.8\times10^2$ ms^{-1} K.E.$=7.1\times10^{21}$ J, Centre of mass $v=2.6\times10^2$ ms^{-1}, K.E.$=6.3\times10^{-21}$ J;
(*b*) Relative $v=5.8\times10^2$ ms^{-1} and K.E.$=2.8\times10^{-22}$ J, Centre of mass 3.0×10^2 ms^{-1} and K.E.$=1.8\times10^{-21}$ J;
(*c*) Relative $v=4.4\times10^2$ ms^{-1}, K.E.$=8.1\times10^{-21}$ J]

9 35. For the reaction, $2B \rightarrow C$, the following data were obtained:

Molar conc. *B*	1.00	0.862	0.758	0.678	0.609
Time (min)	0	500	1000	1500	2000

Determine whether the reaction is first order or second order in *B* and find the specific rate constant.

[**Ans.** Second order, $k=3.20\times10^{-4}$ mole^{-1} min^{-1}.]

9.36. Gaseous ethylamine decomposes as follows:

$$C_2H_5NH_2 \rightarrow C_2H_4 + NH_3$$

At 500°C and an initial $C_2H_5NH_2$ pressure $P_o = 55$ torr in a constant volume vessel, the following data were obtained for the pressure increase $\triangle P$.

t/(min)	1	2	4	8	10	20	30	40
P/(torr)	5	9	17	29	34	47	52	53.5

(*a*) Derive expressions, in terms of t, P_o, $\triangle P$, for one half, first and second order rate constants.

(*b*) Determine which expression from (*a*) best fits data and calculate the rate constant.

[Ans. (*a*) $k_{\frac{1}{2}}=2[P_o^{\frac{1}{2}}-(P_o-\triangle P)^{\frac{1}{2}}]/t$; $k_1=t^{-1}\, ln\, [P_o(P-\triangle P)]$,
$k=\triangle P/[t\, P_o(P_o-\triangle P)]$; (*b*) $k=0.0924$ min^{-1}.]

9.37. Consider the reaction $A+H_2O+H^+$ (aq)→Products. Write the complete rate equation if $C_{H_2O} \geqslant C_A$ and if H^+ is regenerated. If $k'=1.00\times10^{-5}$ s^{-1} for the pseudo first order reaction, find k for the complete rate equation, given that $C_{H_2O}=55.5$ M and $C_{H^+}=0.10$ M.

[**Ans.** 1.80×10^{-6} M^{-1} s^{-1}.]

9.38. At a certain temperature the half-life for the decomposition of Xenon difluoride $XeF_2(g) \rightarrow Xe(g)+F_2(g)$, is 200 seconds when the initial concentration of XeF_2 is 0.01 M and 66.7 seconds when the initial concentration is 0.03 M. What is the order of the reaction and the specific rate constant?

[**Ans.** Second order, $k=0.50$ M^{-1} sec^{-1}.]

9.39. A reaction has the overall stoichiometry $2A+B \rightarrow$ products. The mechanism has been investigated by following the disappearance of *A* and *B* with three different initial concentrations expressed in mole/litre. (*a*) Suggest a mechanism for the reaction. (*b*) Identify the rate-determining step. (*c*) Calculate the rate constant for the rate determining step.

	Exp. 1		*Exp. 2*		*Exp. 3*	
Time, min.	*A*	*B*	*A*	*B*	*A*	*B*
0	0.100	0.100	0.100	0.200	0.050	0.100
1	0.050	0.075	0.050	0.175	0.033	0.092
3	0.025	0.025	0.025	0.1625	0.020	0.085
9	0.010	0.05	0.010	0.1550	0.009	0.080

[**Ans.** (*a*) Reaction mechanism

(*i*) $A+A \xrightarrow[\text{slow}]{k_1}$ Intermediate

(*ii*) [Intermediate] $\xrightarrow[\text{fast}]{}$ Products

(*b*) (*i*) is the rate determining step

(*c*) $k_1 = 10$ litres mole^{-1} min^{-1}.]

9.40. The following data were obtained for the variation of the rate of an enzyme catalysed reaction with temperatures

t°C	2	5	10	15	20	25	30	35
$V_{\max}$ (relative)	1.0	1.49	2.86	5.47	9.97	14.16	18.18	24.05

Construct the Arrhenius plot for this data and comment on your result.
[**Ans.** The plot of $N_{\max}$ against $1/T$ is biphasic. Below 21°C the activation energy is 20.5 k. cal. mole^{-1} whereas above this temperature the activation energy is 9.5 k. cal. mole^{-1}. This indicates that there are two interconvertible forms of enzyme.]

9.41. The following data were obtained for an enzyme catalysed reaction:

t°C	20	28	35	42	50	53
$V_{\max}$ (relative)	1.0	1.88	3.13	5.15	4.22	2.12

Determine the activation energy for the reaction and comment on the data at higher temperatures.
[**Ans.** The plot is linear up to 42°C and gives an activation energy of 57.7 kJ mole^{-1}. Above this temperature there is a sharp fall in $V_{\max}$, this may probably be due to thermal inactivation of the enzyme]

9.42. From the gas viscosity measurements the molecular diameter of H_2 is found to be 2.18×10^{-8} cm. Find the number of collisions per c.c. per sec. at 27°C 1 atm.
[**Ans.** 8.0×10^{28}.]

9.43. The rate constant for the first order decomposition of 2 chloropropane into propylene and hydrogen chloride was found to vary with temperature as follows:

Rate constant $\times 10^3/\text{sec}^{-1}$	0.162	0.238	0.311	0.475	0.706	0.901	1.225	1.593
Temperature/K	640.6	647.7	651.2	657.5	665.1	669.0	674.9	679.7

Calculate the energy of activation and the frequency factor.

[**Ans** .ΔE=211 kJ mole^{-1}, $A=2.5\times10^{-3}$ s^{-1}.]

9.44. When the concentration of A in the simple reaction,

$$A \rightarrow B$$

was changed from 0.502 mole dm^{-3} to 1.007 mole dm^{-3}, the half-life dropped from 51 seconds to 26 seconds at 26°C. What is the order of the reaction and the value of the rate constant?

[**Ans**. Second order, k=0.039 dm^3 mole^{-1} s^{-1}.]

9.45. The rate constant, k, for the alkaline hydrolysis of ethyl iodide was measured at various temperatures as shown.

Temperature/°C	15	30	60	90
10^3 k/dm^3 mole^{-1} s^{-1}	0.0507	0.335	8.13	119

Use a graphical method to calculate the activation energy of the reaction and determine the frequency factor.

[**Ans**. ΔE=90.0 kJ mole^{-1}, $A=1.1\times10^{12}$ dm^3 mole^{-1} s^{-1}.]

9.46. First order rate constants for the decomposition of dinitrogen pentoxide at various temperatures are:

t(°C)	0	25	35	45	55	65
k (s^{-1})	7.9×10^{-7}	3.5×10^{-5}	1.35×10^{-4}	5.0×10^{-4}	1.5×10^{-3}	4.9×10^{-3}

Draw a graph and from it determine the activation energy for the reaction.

[**Ans**. 103 kJ mole^{-1}.]

9.47. Two second order reactions A and B have identical frequency factors. The activation energy of A exceeds that of B by 10.46 kJ mole^{-1}. At 100°C the reaction A is 30 per cent complete after 60 min when the reactant is initially present at a concentration of 0.1 ml dm^{-3}. How long will it take reaction B to reach 70 per cent completion at the same temperature for an initial concentration of 0.05 mole dm^{-3}?

[**Ans**. 1340 s.]

9.48. The Arrhenius equations for the rate of decomposition of methyl nitrite and ethyl nitrite are

$$k_1\ (\text{s}^{-1})=10^{13}\exp\left(\frac{-152300\ \text{J mole}^{-1}}{RT}\right)$$

and
$$k_2\ (\text{s}^{-1})=10^{14}\exp\left(\frac{-157700\ \text{J mole}^{-1}}{RT}\right)$$

respectively. Find the temperature at which the rate constants are equal.

[**Ans**. 282 K.]

9.49. The following data for the first order reaction involving the decomposition of penicillin are obtained from Swintosky *et. al.*

Temperature	First order rate constant, k hr^{-1}
37°C	0.0216
43°C	0.0403
54°C	0.119

Plot the results and calculate the energy of activation and the frequency actor A.

[**Ans**. $E_a \approx$20 k. cal./mole, $A=9.9\times10^{-8}$ sec^{-1}.]

9.50. A drug product is known to be ineffective after it has decomposed 30 per cent. The original concentration of one sample was 5.0 mg/ml When assayed 20 months later the concentration was found to be 4.2 mg/ml. Assuming that decomposition is first order, what should be the expiration time on the level? What is the half-life of this product?

[**Ans.** 41 *mo*, 79.4 *mo*.]

[**Hint:** The drug action at the molecular level for which a convenient model may be constructed assuming that generation of a response by a drug is a rate process.]

10

DISTRIBUTION LAW AND PHASE RULE

INTRODUCTION

When a substance is added to a two-phase liquid mixture, it gets distributed with different equilibrium concentrations in the two phases. The ratio of the concentration of the substance in the two phases is constant, K called the distribution coefficient or partition coefficient.

$$\frac{C_1}{C_2} = K \qquad \ldots (1)$$

where C_1 is the concentration of the solution in phase 1 and C_2 is its concentration in phase 2. It is assumed that the solute neither associates nor dissociates in the liquids i.e., it has the same molecular weight in the two phases.

Case I. When the Solute Associates in One of the Two Solvents

Consider a solute represented by the molecular formula A. Let this solvent exist as such in solvent I and is associated in solvent II as $(A)_n$

$$(A)_n \rightleftharpoons nA \qquad \ldots (2)$$

In this case we have,

$$K = \frac{C_1}{\sqrt[n]{C_2}} \qquad \ldots (3)$$

where n is the degree of association.

Case II. When the Solute Dissociates

(a) When the solute dissociates in solvent I and α_1 is the degree of dissociation of the solute in I.

$$K = \frac{C_1(1-\alpha_1)}{C_2} \qquad \ldots (4)$$

Case III. When the Solute Dissociates in Both the Solvents

In this case the distribution or partition coefficient will take the form,

$$K = \frac{C_1(1-\alpha_1)}{C_2(1-\alpha_2)} \qquad \ldots (5)$$

where α_1 and α_2 are the degrees of dissociation of the solute in solvent *I* and *II* respectively.

Solvent Extraction Method

One of the important applications of distribution law is in the solvent extraction process. The process of extraction is much more economical and efficient if it is carried out in several operations with a given volume of the solvent.

Suppose we have a solution containing W grams of a substance in V_1 c.c. of solution, and suppose that this solution is shaken repeatedly with V_2 c.c. samples of pure immiscible solvent employed for extraction. Then at the end of n extractions, the weight W_n of solute remaining unextracted will be given by

$$W_n = W\left(\frac{KV_1}{KV_1+V_2}\right)^n \qquad \ldots (6)$$

The weight of solute extracted will be,

$$W - W_n = W\left[1-\left(\frac{KV_1}{KV_1+V_2}\right)^n\right] \qquad \ldots (7)$$

where K is the distribution coefficient.

Phase Rule

Phase. A phase is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite boundary surfaces. It is denoted by P.

Component. The number of components for a system is the least number of constituents, which are required to describe the composition of every phase that may be present in any of the equilibrium states of system. It is denoted by C.

Degrees of freedom. The degrees of freedom for a system are defined as the least number of intensive properties that have to be specified to define the equilibrium state of this system. It is denoted by F.

Phase rule is a law of equilibrium state and is not applicable unless the equilibrium among the different phases has been reached. It may be stated as

$$F = C - P + 2 \qquad \ldots (8)$$

Solid-liquid diagrams. There are several features that may appear on these diagrams, such as partial, complete or no mutual solubility of solids, congruent, incongruent or no compound formation; and solid-solid phase transitions.

It is of interest to apply the phase rule to the freezing of a solution consisting of a solvent specification of only one and one solute. At temperature at which vapour pressure curve of the solution intersects the sublimation pressure curve of the solvent, crystals appear. Thus, there are two components and three phases in the system, solution, solid solvent, and vapour.

$$F=C-P+2$$
$$F=2-3+2$$
$$F=1$$

Hence, specification of one variable (temperature, vapour pressure of concentration) will define the system. As the temperature is lowered further, crystallization of solvent continues, and the solution phase becomes more concentrated until finally a saturated solution is obtained. At this point, both solute and solvent crystallize simultaneously, and there are four phases:

$$F=2-4+2$$
$$F=0$$

The system is invariant. There will be a simultaneous crystallization of solvent and solute at constant temperature until all the liquid solution is solidified. The mixture which solidifies under these conditions is called a eutectic mixture and the constant temperature at which this solidification takes place is called the eutectic temperature or eutectic point. This is shown in Fig. 10.1.

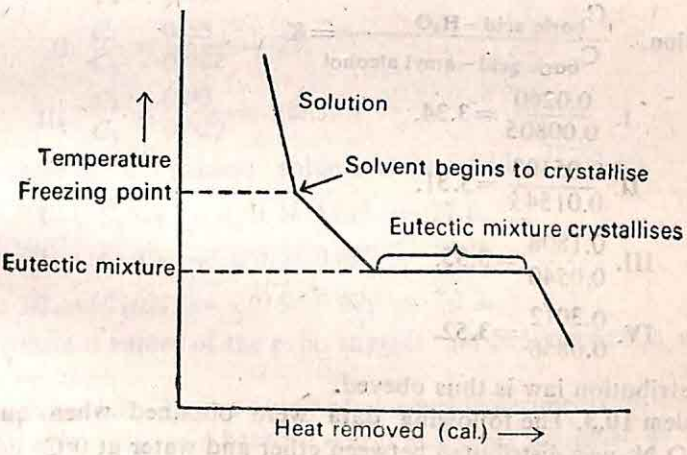


Fig. 10.1. Cooling curve for a solution containing a single solute.

Problem 10.1. The concentration of iodine between water and CCl_4 is as under:

CI_2-H_2O 0.000321 0.000503 0.00764 0.00115

$C_{I_2-CCl_4}$ 0.002745 0.0429 0.06541 0.0101

Show that these results illustrate distribution law.

Solution. I. $\frac{C_{I_2-H_2O}}{C_{I_2-CCl_4}}=\frac{0.000321}{0.02745}=0.0117.$

II. $\frac{C_{I_2-H_2O}}{C_{I_2-CCl_4}}=\frac{0.000503}{0.0429}=0.0117.$

III. $\frac{C_{I_2-H_2O}}{C_{I_2-CCl_4}}=\frac{0.00764}{0.06541}=0.0117.$

IV. $\frac{C_{I_2-H_2O}}{C_{I_2-CCl_4}}=\frac{0.00115}{0.0101}=0.0114.$

Problem 10.2. In a distribution experiment the results of distribution of boric acid between water and amyl alcohol are as under:

Concentration of boric acid in H_2O	0.0260	0.05103	0.1808	0.3012
Concentration of boric acid in amyl alcohol	0.00805	0.01545	0.0540	0.0856

Show that distribution law is obeyed.

Solution. $\frac{C_{\text{boric acid}-H_2O}}{C_{\text{boric acid}-\text{amyl alcohol}}}=K$

I. $\frac{0.0260}{0.00805}=3.34.$

II. $\frac{0.05103}{0.01545}=3.31.$

III. $\frac{0.1808}{0.0540}=3.35.$

IV. $\frac{0.3012}{0.0856}=3.52.$

The distribution law is thus obeyed.

Problem 10.3. The following data were obtained when quinine, $C_{20}H_{24}O_2N_2$ was distributed between ether and water at 0°C

C_1 (concentration in water layer)	0.0547	0.0590	0.0622
C_2 (concentration in ether layer)	1.1142	1.2901	1.4281

If quinine exists as monomer in water, determine its molecular complexity in ether.

Solution. I. $\frac{C_1}{C_2} = \frac{0.0547}{1.1142} = 0.0490.$

II. $\frac{C_1}{C_2} = \frac{0.0590}{1.2901} = 0.0457.$

III. $\frac{C_1}{C_2} = \frac{0.0622}{1.4281} = 0.0437.$

Quinine exists as misnomer in ether.

Problem 10.4. When benzoic acid was shaken with mixtures of benzene and water at a constant temperature, the following results were obtained.

	I	II	III
Equilibrium concentration of benzoic acid in benzene (C_1)	0.24	0.55	0.93
Equilibrium concentration of benzoic acid in water (C_2)	0.015	0.022	0.029

Comment on these results.

Solution. First calculate the ratio, $\frac{C_1}{C_2}$

I. $\frac{C_1}{C_2} = \frac{0.24}{0.015} = 16.$

II. $\frac{C_1}{C_2} = \frac{0.55}{0.022} = 25.$

III. $\frac{C_1}{C_2} = \frac{0.93}{0.029} = 32.$

Since these are not constant values, let us calculate $\sqrt{C_1/C_2}$

I. $\sqrt{C_1}/C_2 = \sqrt{0.24}/0.015 = 32.6.$

II. $\sqrt{C_1}/C_2 = \sqrt{0.55}/0.022 = 33.7.$

III. $\sqrt{C_1/C_2} = \sqrt{0.93/0.029} = 33.2.$

The constant values of the ratio suggest that benzoic acid is associated in benzene.

Problem 10.5. Results obtained in some experiments on the distribution of succinic acid between water and ether are given as under:

$C_{1(H_2O)}$	0.191	0.370	0.547	0.749
$C_{2(ether)}$	0.0248	0.0488	0.0736	0.101

Calculate the distribution coefficient of succinic acid between water and ether

$$K = C_1/C_2$$

$$\text{I. } K=\frac{0.191}{0.0248}=\frac{1910}{248}=7.70.$$

$$\text{II. } K=\frac{0.370}{0.0488}=\frac{370}{488}=7.50.$$

$$\text{III. } K=\frac{0.547}{0.0736}=\frac{5470}{736}=7.43.$$

$$\text{IV. } K=\frac{0.749}{0.101}=\frac{749}{101}=7.41.$$

Problem 10.6. A solution of hydrogen peroxide in amyl alcohol contains 20 grams of hydrogen peroxide in 200 ml. It is to be extracted with 200 ml of water (*a*) when used in two lots of 100 ml each, and (*b*) in one lot. Calculate the amount of hydrogen peroxide extracted in each case. Given that the partition coefficient of hydrogen peroxide between amyl alcohol and water is $\frac{1}{7}$.

Solution. (*a*) Amount of solute extracted when extraction is done in two lots

$$W_n=W\left[1-\left(\frac{KV_1}{KV_1+V_2}\right)^n\right]$$

$$W_n=20\left[1-\left(\frac{\frac{1}{7}\times 200}{\frac{1}{7}\times 200+100}\right)^2\right]$$

$$W_n=20\left[1-\left(\frac{200}{7}\times\frac{7}{900}\right)^2\right]$$

$$W_n=20\left[1-\frac{4}{81}\right]$$

$$W_n=\frac{1540}{81}=19.01\text{ gm.}$$

Hence when extraction is done in two lots the amount extracted is 19.01 gm.

(*b*) Amount of solute extracted when extraction is done in one lot only.

$$W_n=W\left[1-\left(\frac{KV}{KV_1+nV_2}\right)\right]$$

$$W_n=20\left[1-\left(\frac{\frac{1}{7}\times 200}{\frac{1}{7}\times200+200}\right)\right]$$

$$W_n=20\left[1-\frac{200}{7}\times\frac{7}{1600}\right]$$

$$W_o = 20 \times \frac{7}{8} = \frac{35}{2} = 17.5 \text{ gm.}$$

The amount extracted when extraction is done in one lot will be 17.5 gm.

Problem 10.7. The solubility of a substance X is three times as great in other liquids than in water. Compare the quantities of the substance extracted from 100 ml of aqueous solution by (*a*) 100 ml of ether in one operation, (*b*) two extractions using 50 ml in each extraction. Calculate the amount of substance unextracted in each case.

Solution. (*a*) The amount of X unextracted using 100 ml in one lot

$$W_n = \left(\frac{KV}{KV+100}\right)W$$

$$W_n = \left(\frac{\frac{1}{3}\times 100}{\frac{1}{3}\times 100+100}\right)W$$

$$W_n = \frac{100}{3}\times\frac{3}{400}\,W = 25 \text{ per cent.}$$

(*b*) The amount of X unextracted using 50 ml in each lot and extraction is done twice.

$$W'_n = W\left(\frac{KV}{KV\times v}\right)^n$$

$$W'_n = W\left(\frac{\frac{1}{3}\times 100}{\frac{1}{3}\times 100+50}\right)^2$$

$$W'_n = W\left(\frac{100}{3}\times\frac{3}{250}\right)^2$$

$$W'_n = \frac{4}{25}W = 16 \text{ per cent.}$$

Problem 10.8. 100 cm³ of an aqueous solution contains 10 g of an organic nitrophenol. Calculate the weight of nitrophenol extracted by 100 cm³ of ethoxy-ethane, used (*a*) in one extraction, (*b*) in four separate extractions using 25 cm³ of ethoxy-ethane for each extraction. The partition coefficient of the nitrophenol between ethoxy-ethane and water is 3 : 1 at room temperature.

Solution. (*a*) Amount of solute extracted in one lot using 100 cm³ will be,

$$W'_n = W\left[1-\left(\frac{KV_1}{KV_1+V_2}\right)\right]$$

$$W'_n = 10\left[1-\left(\frac{\frac{1}{3}\times 100}{\frac{1}{3}\times 100+100}\right)\right]$$

$$W'_n=10\left[1-\frac{100}{3}\times\frac{3}{400}\right]$$

$$W'_n=10\times\frac{3}{4}$$

$$W'_n=7.5 \text{ g.}$$

(*b*) Amount of solute extracted at the end of fourth step,

$$W'_n=W\left[1-\left(\frac{KV_1}{KV_1+V_2}\right)^n\right]$$

$$W'_n=10\left[1-\left(\frac{\frac{1}{3}\times 100}{\frac{1}{3}\times 100+25}\right)^4\right]$$

$$W'_n=8.93 \text{ g.}$$

Problem 10.9. The partition coefficient of a substance between chloroform and water is approximately 5 : 1. Show that the amount of substance extracted from 100 c.c. of an aqueous solution is more by using 50 c.c. chloroform at a time in two instalments than using 100 c.c. of it at a time.

Solution. (*a*) Extraction is done twice using 50 c.c. each time. Let W be the amount of substance being present in the aqueous solution and the extraction is done using 50 c.c. of chloroform at a time in two instalments.

Amount of solute extracted $W_n=W\left[1-\left(\frac{KV_1}{KV_1+V_2}\right)^2\right]$

where $K=\frac{1}{5}$

$$W_n=W\left[1-\left(\frac{\frac{1}{5}\times 100}{\frac{1}{5}\times 100+50}\right)^2\right]$$

$$W_n=W\left[1-\left(\frac{100}{5}\times\frac{5}{350}\right)^2\right]$$

$$W_n=W\left[1-\frac{4}{49}\right]=\frac{45}{49}W.$$

(*b*) Extraction is done in one lot using 100 c.c. The amount of solute extracted,

$$W'_n=W\left[1-\left(\frac{KV_1}{KV_1+nV_2}\right)\right]$$

$$W'_n=W\left[1-\left(\frac{\frac{1}{5}\times 100}{\frac{1}{5}\times 100+100}\right.\right]$$

$$W'_n=W\left[1-\frac{100\times 5}{5\times 600}\right]$$

$$W'_n = \frac{5}{6} W$$

Since $$\frac{45W}{49} > \frac{5}{6} W.$$

Hence the amount of solute extracted is more when extraction is done in two instalments than when it is done in one instalment.

Problem 10.10. Acetic acid was shaken with CCl_4 and H_2O. The following results were obtained :

$C_1(H_2O)$	5.02	7.98	10.90
$C_2(CCl_4)$	0.292	0.724	1.41

Assuming that acetic acid has single molecules in water show that it has double molecules in CCl_4

$$\text{I. } K = \frac{C_1}{\sqrt{C_2}} = \frac{5.02}{\sqrt{0.292}} = 9.29.$$

$$\text{II. } K = \frac{C_1}{\sqrt{C_2}} = \frac{7.98}{\sqrt{0.724}} = 9.38.$$

$$\text{III. } K = \frac{C_1}{\sqrt{C_2}} = \frac{10.90}{\sqrt{1.41}} = 9.18.$$

The constant value for K indicates that acetic acid exists as double molecules in CCl_4.

Problem 10.11. Experiments on the study of the distribution ratio of phenol between water and chloroform gave the following results:

Concentration in $H_2O(C_1)$	0.094	0.163	0.254	0.436
Concentration in chloroform (C_2)	0.254	0.761	1.85	5.43

What conclusions can be drawn from these results regarding the molecular condition of phenol in chloroform?

Solution. Phenol in chloroform may be present either as normal molecules or as associated molecule.

$$\text{I. } \frac{C_1}{C_2} = \frac{0.094}{0.254} = 0.3701.$$

$$\text{II. } \frac{C_1}{C_2} = \frac{0.163}{0.761} = 0.2142.$$

$$\text{III. } \frac{C_1}{C_2} = \frac{0.254}{1.85} = 0.1373.$$

$$\text{IV. } \frac{C_1}{C_2} = \frac{0.436}{5.43} = 0.0833.$$

Since the C_1/C_2 is not constant. Hence phenol does not exist in the form of normal molecules.

$$\text{I. } \frac{C_1}{\sqrt{C_2}} = \frac{0.094}{\sqrt{0.254}} = 0.1865.$$

$$\text{II. } \frac{C_1}{\sqrt{C_2}} = \frac{0.163}{\sqrt{0.761}} = 0.1868.$$

$$\text{III. } \frac{C_1}{\sqrt{C_2}} = \frac{0.254}{\sqrt{1.85}} = 0.1867.$$

$$\text{IV. } \frac{C_1}{\sqrt{C_2}} = \frac{0.436}{\sqrt{5.43}} = 0.1870.$$

Since $\frac{C_1}{\sqrt{C_2}}$ is constant phenol exists as dimer or double molecules in chloroform.

Problem 10.12. Determine the number of components in the following systems: (*a*) An aqueous solution of KCl; (*b*) a mixture of $CaCO_3(s)$, $CaO(s)$, and $CO_2(g)$; (*c*) $FeSO_4.H_2O(s) = FeO(s) + H_2SO_4$.

Solution. (*a*) Here the amounts of H_2O and KCl will define the system completely, even though the other species such as $K^+(aq.)$, $Cl^-(aq.)$, $H^+(aq.)$ and $OH^-(aq.)$ are present. The number of components in this will be two.

(*b*) The least number of concentration terms needed to define the system is 2, as there is a following equilibria in the system

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g).$$

The concentration of any two species need be known to define the system. Hence the number of components is two.

(*c*) The concentrations of three components is required to define the system completely, i.e., one gaseous and two solid species. Hence the number of components of the system is three.

Problem 10.13. The break and halt temperatures for the cooling curves of melts of metals *A* and *B* are given in the Table below.

Mole per cent A	*First break (°C)*	*First halt (°C)*	*Second halt (°C)*
100		1100	
90	1060	700	
80	1000	700	
70	940	700	400
60	850	700	400
50	750	700	400
40	670	400	
30	550	400	
20		400	
10	450	400	
0		500	

Construct a phase diagram and label the phase regions. Give the probable formula of any compounds.

Solution. Here each halt corresponds to a line of three-phase equilibrium and each break to a boundary between a one-phase and a two-phase region. This simplest diagram is shown in Fig. 10.2. Here an unstable compound is indicated that must contain less than 80 per cent and more than 70 per cent *A*, since it is between these limits that the lower three phase lines appear. However, a good guess appears to be 75 per cent *A* which corresponds to the formula A_3B.

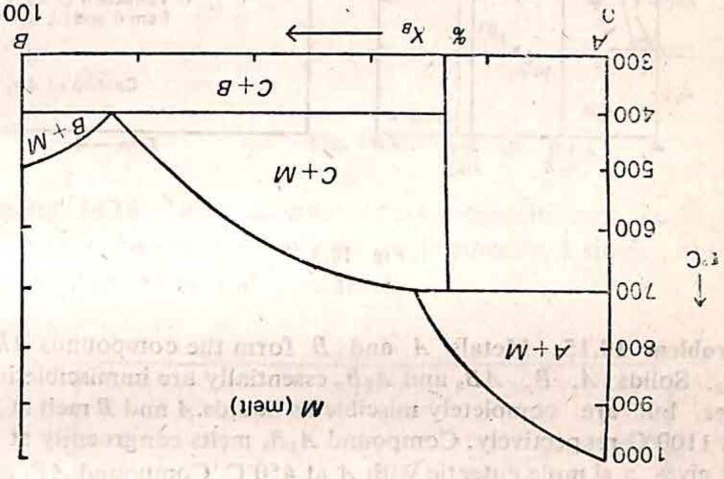


Fig. 10.2.

Problem 10.14. *A* and *B* form two solid compounds. A_2B melts at 800°C to a liquid having composition A_2B. AB_2 decomposes at 700°C to solid *B* and a liquid phase. The melting point of *A* is 500°C; of *B*, 1000°C. No solid solutions are formed.

(*a*) Sketch the temperature—mole fraction phase diagram for the system *A*—*B*. Label each region.

(*b*) A liquid solution containing 70 mole per cent *B* is cooled slowly from 1100 to 400°C. Draw a graph showing temperature as a function of time in this cooling process. Show how each major feature of the cooling curve is related to the phase diagram.

Solution.

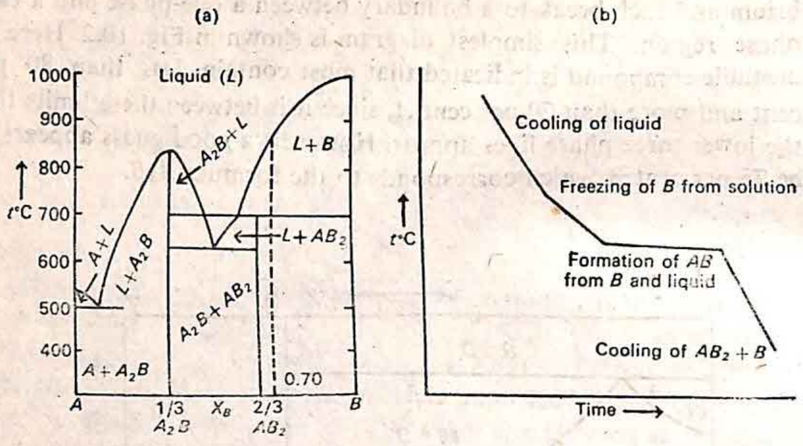


Fig. 10.3.

Problem 10.15. Metals A and B form the compounds AB_3 and A_2B_3. Solids A, B, AB_3 and A_2B_3 essentially are immiscible in each other, but are completely miscible as liquids. A and B melt at 600°C and 1100°C respectively. Compound A_2B_3 melts congruently at 900°C and gives a simple eutectic with A at 450°C. Compound AB_3 decomposes at 800°C to give the other compound and a melt. There is a eutectic at 650°C.

(*a*) Draw the simplest phase diagram consistent with this information and label all phase regions.

(*b*) Sketch cooling curves for melts of composition 90 per cent A and 30 per cent A. and label as to phases appearing or disappearing at each break and halt.

Solution.

The composition of the first eutectic melt could be either right or the left of the 90 per cent composition point. If it lay to the left, the order of appearance of A and C_1, would be the reverse of that shown in the cooling curve.

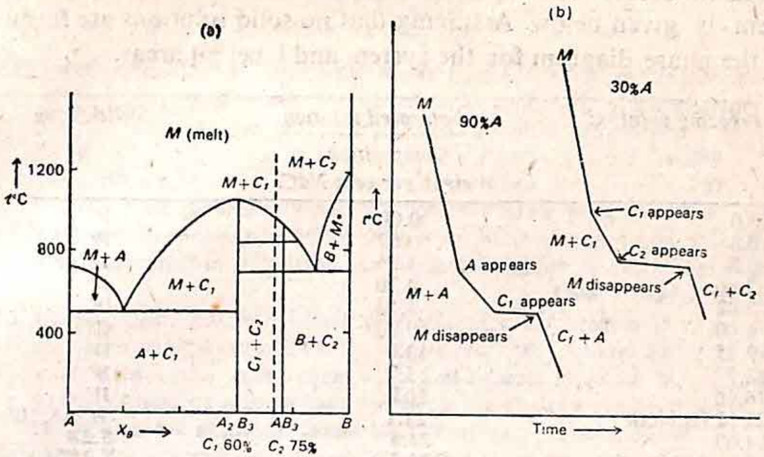


Fig. 10.4.

Problem 10.16. Draw a temperature-composition phase diagram for a binary system *A-B* having a single eutectic, a single peritectic and no solid solutions. Label all areas.

Solution.

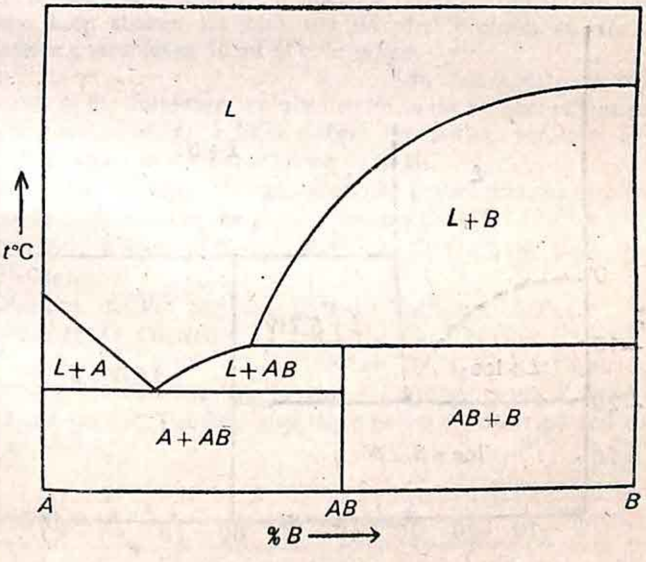


Fig. 10.5.

Problem 10.17. The data for the sodium chloride (S) water (W) system is given below. Assuming that no solid solutions are formed, plot the phase diagram for the system and label all areas.

Freezing point °C	*Saturated solution*	*Solid phase*
	Composition, Weight per cent NaCl	
0.0	0.00	W
−0.4	0.69	W
−0.8	1.35	W
−2.86	4.70	W
−3.42	5.53	W
−6.60	9.90	W
−9.25	13.0	W
−12.7	16.7	W
−16.66	20.0	W
−21.12 (eutectic)	23.1	$W+S.2W$
−14.00	24.6	$S.2W$
+ 0.1 (peritectic)	26.3	$S.2W+S$
10.0	26.34	S
15.0	26.34	S
20.0	26.40	S
30.0	26.52	S
40.0	26.67	S
60.0	27.07	S
80.0	27.55	S
100.0	28.15	S

Solution.

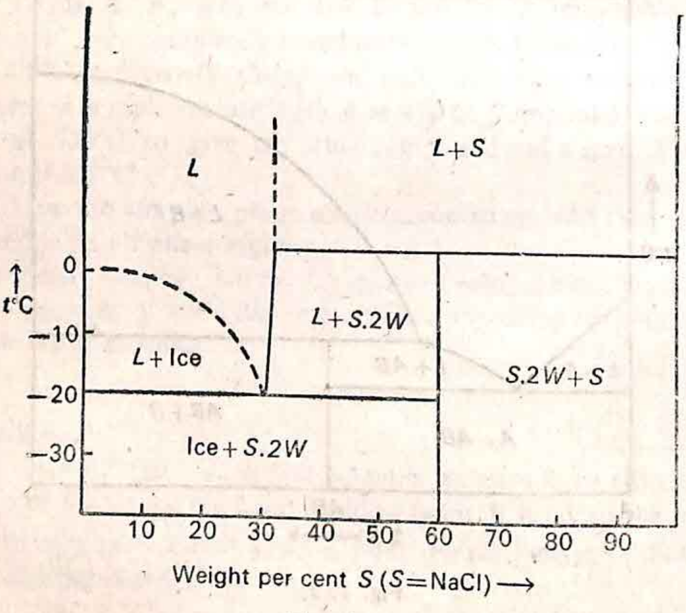


Fig. 10.6.

EXERCISES

10.1. Succinic acid has its normal molecular weight in water. In the distribution of the acid between water and benzene, the concentrations in the aqueous and the benzene layers were found to be C_1 and C_2 respectively

C_1 (g/100 c.c.)	0.150	0.195	0.289
C_2 (g/100 c.c.)	2.420	4.120	9.700

Calculate the molecular weight of succinic acid in benzene. [**Ans.** 236.]

10.2. Partition coefficient of a solute Z between two solvents A and B is 16. If solubility of Z in B is 50 mg per 100 c.c. Calculate the solubility of Z in A. [**Ans.** 800 mg/100 c.c.]

10.3. Benzoic acid distributes itself between water and benzene in such a way that in a definite volume of water there are 1.50, 1.95 and 2.97 g of benzoic acid while in an equal volume of benzene there are 24.2, 41.2 and 97.0 g of benzoic acid. What conclusion can be drawn from these results concerning the molecular condition of benzoic acid in benzene?
[**Ans.** Benzoic acid is associated in benzene with molecular weight double than the normal molecular weight.]

10.4. The partition coefficient of a substance Y between ether and water is 3, Y being more soluble in ether. 100 ml of an aqueous solution containing 10 g of Y is shaken with (*a*) 100 ml of ether and (*b*) four successive quantities of 25 ml of ether. Calculate the weight of Y left in the aqueous solution in each of the two experiments. [**Ans.** (*a*) 2.5 g, (*b*) 1.07 g.]

10.5. The partition coefficient of an alkaloid between chloroform and water is 20, the alkaloid being more soluble in chloroform. Compare the weights of the alkaloid remaining in the aqueous solution after 100 ml containing 1 g has been shaken (*a*) with 100 ml of chloroform, and (*b*) with two successive quantities of 50 ml of chloroform.
[**Ans.** (*a*) 0.048 g, (*b*) 0.0083 g.]

10.6. For each of the following systems determine the number of components:
- (*a*) $NH_4Cl(s)$, $NH_3(g)$, $HCl(g)$, where the partial pressure of NH_3 is always equal to the partial pressure of HCl.
- (*b*) $NH_4Cl(c)$, $NH_3(g)$, $HCl(g)$ where the partial pressure of NH_3 is not necessarily equal to the partial pressure of HCl.
- (*c*) NaCl(c), KBr(c), K^+(aq), Na^+(aq.), Cl^-(aq.), Br^-(aq.), H_2O(liq.) H_2O(g).
- (*d*) NaCl(c), KCl(c), Na^+(aq.), Cl^-(aq.), H_2O(liq.), H_2O(g).
- (*e*) $CaCl_2.6H_2O$, Ca^{2+}(aq.), Cl^-(aq.), H_2O(liq.), H_2O(g).

[**Ans.** (*a*) 1, (*b*) 2, (*c*) 4, (*d*) 3, (*e*) 2.]

10.7. A certain substance exists in two solid forms Q and R, as well as the liquid and vapour. The following triple points are observed and all equilibria are stable.

Temperature, °C	*Pressure, aim,*	*Phases*
10	1.0	Q, R, vapour
80	10.0	R, liquid, vapour
50	1000.0	Q, R, liquid

(*a*) Sketch the pressure-temperature phase diagram for the substance. Indicate the phase or phases present in each region.

(*b*) In each pair select the form with greater density in the vicinity of 50°C and 100 if you have enough information to decide, *Q* and *R*, *R* and liquid; *Q* and liquid. If you cannot decide, explain the reason.

[**Ans.** We cannot decide about *Q* and liquid because we do not know whether the *Q*-liquid equilibrium line has a positive slope.

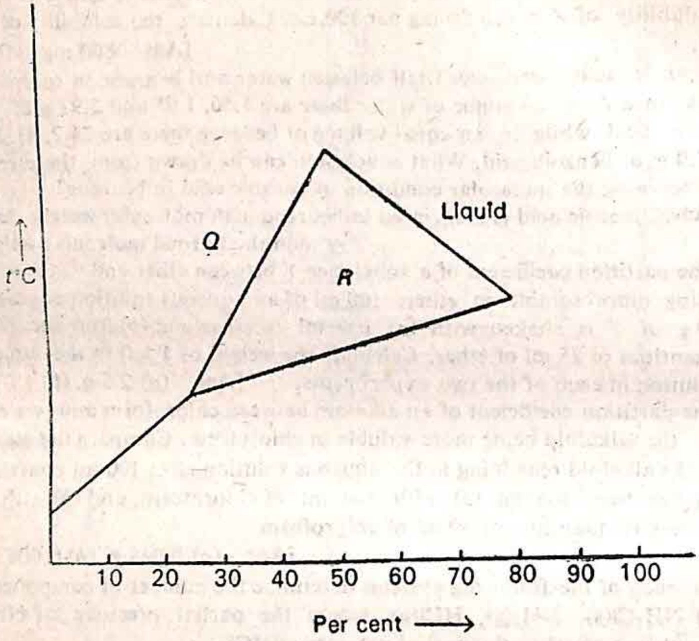


Fig. 10.7.

10.8 For the system shown in the Fig. 10.8, prove that at equilibrium

$$\frac{W_1}{W_2} = \frac{x_2 - x_T}{x_T - x_1}$$

where W_1=the weight of phase 1, W_2=the weight of phase 2, x_1=the weight of per cent of *B* in phase 1, x_2=the weight of per cent of *B* in phase 2, x_T =weight per cent of *B* in the total system.

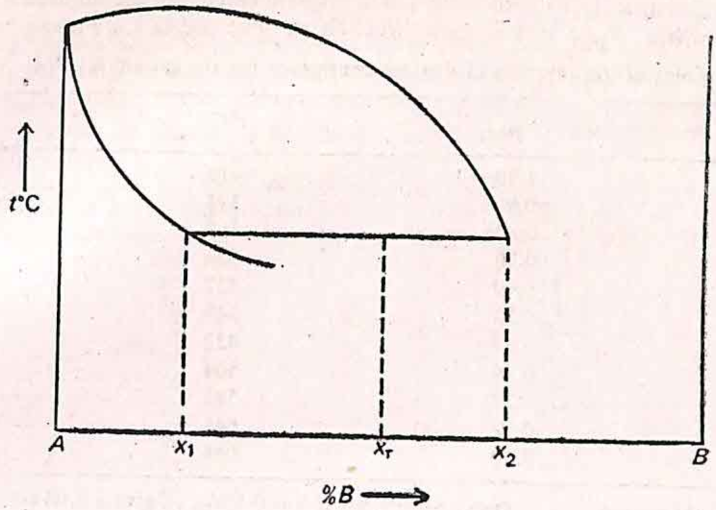


Fig. 10.8.

10.9. The phase diagram of the system composed of the two partially miscible liquids A and B is given. 30 g of pure A is mixed with 70 g of pure B.

(*a*) What will be the boiling point of this mixture at 1 atm?

(*b*) What is the maximum amount of pure B recoverable by fractional distillation only?

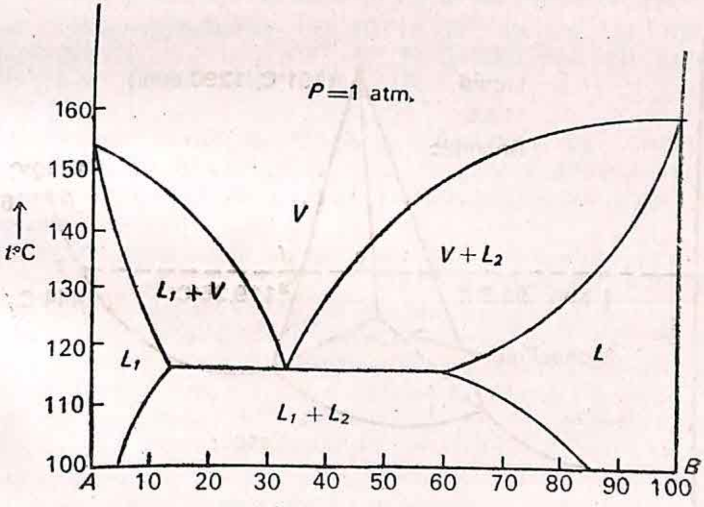


Fig. 10.9.

[Ans. (*a*) 118°C, (*b*) 51 g of pure *B*.]

10.10. Construct and interpret the phase diagram based on the following data where N_{PbI_2} is the mole fraction of lead iodide and t is the freezing point of the solution in degrees centigrade for the system KI-PbI_2.

N_{PbI_2}	t°C
1.00	412
0.90	395
0.80	367
0.70	324
0.60	337
0.50	349
0.40	422
0.30	504
0.20	585
0.10	641
0.00	686

Assuming that all compositions are below 0.5 N_{PbI_2}, give a final solidification temperature of 346°C.

[**Ans.** Compound KI-PbI_2 melting point 349°C, Eutectics at 0.47 N_{PbI_2} and 346° and 0.7 N_{PbI_2} and 324°.]

10.11. Consider the phase diagram for sulphur as shown in the Fig. 10.10. The diagram does not show various transitions that occur in the liquid state as the S_8 molecules become fragmented.

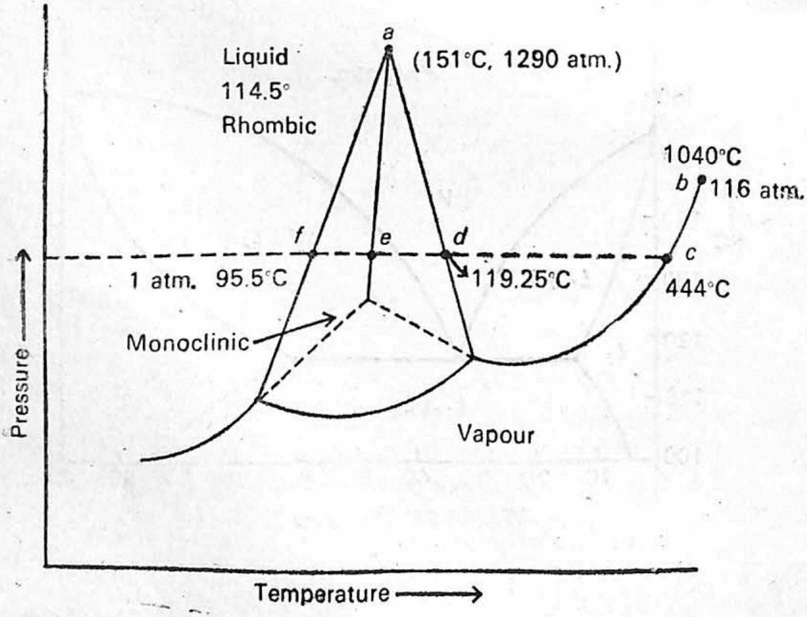


Fig. 10.10.

(*a*) What is the stable form of sulphur under room conditions?

(*b*) Suppose a sample of S were dissolved in CS_2 and the solvent evaporated. What would be the stable form of sulphur?

(*c*) What would be observed if molten sulphur at 115°C were poured into boiling water? [Ans. (*a*) rhombic, (*b*) rhombic, (*c*) monoclinic.]

10.12. The following data are given by Andrews for the system *o*-dinitrobenzene-*p*-dinitrobenzene:

Mole per cent of p-dinitrobenzene	*Initial melting point, °C*
100	173.5
90	167.7
80	161.2
70	154.5
60	146.1
50	136.6
40	125.2
30	111.7
20	104.0
10	110.6
0	116.9

Construct a temperature-composition diagram for the system. Find graphically the maximum percentage of *p*-dinitrobenzene which can be recovered pure by crystallization from mixtures of the two compounds containing originally 95 per cent of the paracompound. [Ans. 98.4 per cent.]

10.13. The temperatures at which solid first crystallizes out when liquid mixtures of benzophenone and diphenylamine are cooled are given as follows:

Mole per cent diphenylamine	0	10	20	30	40	50	60	70	80
Temperature, °C	47	42	34	35	38.5	40.0	37.0	34.0	41.0
Mole per cent diphenylamine	90	100							
Temperature, °C	48	53							

Draw a temperature-composition diagram and label each region indicating which phases are in equilibrium under the conditions that the regions represent. What conclusions can be drawn from the nature of the phase diagram?

[Ans. An addition compound $(C_6H_5)_2CO(C_6H_5)_2NH$ with a congruent melting point of 40°C is formed.]

10.14. Antimony (melting point 630°C) and lead (melting point 326°C) form one eutectic mixture at 246°C which is 81 mole per cent lead, but do not form any solid solutions. Draw a temperature-composition diagram, assuming that the liquid's lines are linear. Label each region and indicate which phases are in equilibrium under the conditions that the regions are present. For a mixture containing 50 mole per cent lead, determine (*a*) the temperature at which solid first crystallizes out, and (*b*) the proportion of the eutectic in the mixture at 200°C.

[Ans. (*a*) 393°C, (*b*) 61.7 mole per cent.]

10.15. Sketch the phase diagram for thallium and mercury with freezing points plotted against per cent by weight. Use the following facts about the system:

Mercury melts at −39°C: the compound Tl_2Hg_5 melts at 15°C; Tl melts at 303°C. Tl lowers the freezing point of mercury down to a minimum of −60°C at a composition of 8 per cent by weight Tl. The eutectic point for Tl and Tl_2Hg_5 is 0.4 at a composition corresponding to 41 per cent by weight Tl. Label the phases present and state the variance at each area and eutectic point. [**Ans.** In the liquid region $F=2$, in the two-phase regions, $F=1$, and at the eutectic point $F=0$.]

10.16. The phase diagram for magnesium-copper at constant pressure shows that two compounds are formed: $MgCu_2$ which melts at 800°C, and Mg_2Cu which melts at 580°C. Copper melts at 1085°C and Mg at 648°C. The three eutectics are at 9.4 per cent by weight Mg (680°C) 34 per cent by weight Mg (560°C) and 65 per cent by weight Mg (380°C). Construct the phase diagram. State the variance for each area and eutectic point.
[**Ans.** In the liquid region $F=2$, in the two-phase regions $F=1$, and at the eutectic points $F=0$]

10.17. The following data are obtained by cooling solutions of magnesium and nickel.

Ni, weight per cent	0	10	28	38	60	83	88	100
Inflection in cooling curve °C	—	608	—	770	1050	—	—	—
Plateau in cooling curve °C	—	651	510	510	770	1180	1080	1450

It is found that in addition cooling solutions containing between 28 per cent and 38 per cent Ni deposit Mg_2Ni, whereas solutions containing between 38 per cent and 82 per cent Ni deposit $MgNi_2$. Plot the phase diagram.

11

ELECTROCHEMISTRY

One of the most important single steps in establishing the electrical nature of the forces between atoms was the electrolysis experiments by Michael Faraday in 1833. He made two quantitative observations, now called Faraday's laws:

1. The weight of chemical substance produced in an anode or cathode reaction in an electrolysis cell is proportional to the quantity of electricity passed through the cell.

2. The weights of two different substances produced by the same quantity of electricity are proportional to the equivalent weights of the substances in reactions between them or with other substances. One mole of electrons will have a total charge of

$$=1.6021\times10^{-19}\text{ coulomb}\times6.022\times10^{23}\text{ mole}^{-1}$$
$$=96{,}487\text{ coulomb mole}^{-1}.$$

This is called one Faraday, denoted by F.

Faraday's laws have both the practical and theoretical significance. The discharge at a cathode of formation at anode, of 1 g equivalent of any ion requires the passage of one Faraday of electricity. The quantity $\frac{F}{N}=\epsilon$ gives the value of the unit charge on the electron.

Specific conductance. It is denoted by the symbol $\varkappa$ (kappa) and is defined as

$$\varkappa=\left(\frac{l}{a}\right)\times\frac{1}{R} \qquad \ldots(1)$$

where l is the distance in cm between the electrodes, a is their area of cross-section in sq. cm, and R is resistance is ohms.

Units of specific conductance: ohms^{-1} cm^{-1} or mhos cm^{-1}.

Equivalent conductance. It is denoted by the symbol Λ (lambda) and is defined by

$$\Lambda=\left(\frac{l}{a}\right)\frac{1}{R}\times\frac{1000}{C} \qquad \ldots(2)$$

where C is the concentration of the solution in gram equivalents per litre. It is the conductance due to all ions present in a solution containing 1 g equivalent of an electrolyte.

Units of equivalent conductance: $\text{Ohm}^{-1}\ \text{cm}^2\ \text{equiv.}^{-1}$

Molecular conductance. It is denoted by the symbol μ (mu). It is the conductance due to all ions present in a solution containing 1 mole of electrolyte.

Degree of dissociation of a weak electrolyte. It is equal to the ratio of equivalent conductivity at any concentration to the equivalent conductivity Λ_o at infinite dilution, i.e.,

$$\alpha = \frac{\Lambda}{\Lambda_o} \qquad \ldots (3)$$

Kohlrausch gave an empirical relationship between the equivalent conductance of an electrolyte at infinite dilution Λ_o and equivalent ionic conductivities of the anion and cation

$$\Lambda_o = \lambda^+{}_o + \lambda^-{}_o \qquad \ldots (4)$$

$\lambda_o{}^+$ and $\lambda_o{}^-$ are the ionic conductances at infinite dilution of the cation and anion respectively.

Determination of solubilities by conductance measurements. The conductance measurements can be used to determine the solubilities of simple sparingly soluble electrolytes. It is the solubility in gram equivalent per litre of a gram salt and $\varkappa$ is the specific conductance of the saturated solution, then the equivalent conductance Λ is given by,

$$\Lambda = \frac{1000\ \varkappa}{s} \qquad \ldots (5)$$

In case of a sparingly soluble salt the saturated solution will be so dilute that Λ will be nearly equal to Λ_o, the equivalent conductance at infinite dilution

$$\Lambda_o = 1000 \frac{\varkappa}{s} \qquad \ldots (6)$$

or

$$s = \frac{1000\ \varkappa}{\Lambda_o} \qquad \ldots (7)$$

Since the conductance of water is appreciable, the conductance of solute will be given by

$$\varkappa_{solute} = \varkappa_{solution} - \varkappa_{water} \qquad \ldots (8)$$

Transference number. During electrolysis, ions of the electrolyte migrate to oppositely charged electrodes. The ability of an electrolyte to conduct electricity is dependent upon the product of the total charge carried by the ion, multiplied by the velocity of the ion under the influence of electric field between the electrodes.

Current carried by an ion is proportional to the speed of that ion, so the total current carried is proportional to the sum of speeds of the two ions, i.e.,

$$t_c \propto U_c \text{ (speed of the cation)}$$

$$t_a \propto U_a \text{ (speed of the anion)}$$

$$(t_a+t_c) \propto (U_c+U_a) \quad \ldots (9)$$

The fraction of the current carried by an ion is called its transport number. It is denoted by t_c or t_+ the transport number of the cation, t_a or t_- the transport number of the anion.

$$t_c = \frac{\text{Current carried by cation}}{\text{Total current carried}}$$

$$t_c = \frac{U_c}{U_c+U_a}$$

$$t_c = \frac{\text{Decrease in concentration around anode}}{\text{Total decrease in concentration around both the electrodes.}}$$

Similarly

$$t_a = \frac{U_a}{U_c+U_a}$$

$$t_a = \frac{\text{Decrease in concentration around cathode}}{\text{Total decrease in concentration around both the electrodes}} \quad \ldots (10)$$

Thus the transference number of an ion can be determined by determining the change in concentration around an electrode and the amount discharged at any electrode or the number of equivalent of current passed. In order to determine the number of equivalents of current passed, a coulometer is generally included in the circuit as the experimental solution, so that the same quantity of electricity passes through the same circuit. Hittorf's method provides a simple method for its determination.

Sometimes ions discharged around an electrode attack and dissolve it. In such cases there is an apparent increase of concentration around the electrode. Here the amount of the ion dissolved from an electrode is equal to the amount deposited at the other electrode.

The moving boundary method. The Hittorf method is less accurate for fairly dilute solutions, this is because small concentration changes occur when the current is passed. It has, therefore, been replaced by moving boundary method. According to this method the transport number t_+ of a cation is given by the relation.

$$t_+ = \frac{l \times a \times F \times c}{Q} \quad \ldots (11)$$

where l is the distance through which the boundary moves, a is the area of cross-section of the tube, F is Faraday, c is the concentration in gram equivalents per c.c. and Q is the coulombs of electricity passed.

Problem 11.1. Exactly 200,000 coulombs of electricity are passed through the electrolysis cell containing copper sulphate solution that is designed to purify copper electrolytically. How much copper will plate on the cathode?

Solution. The number of Faradays or moles of electrons, is

$$\frac{200{,}000 \text{ coulombs}}{96{,}487 \text{ coulombs mole}^{-1}} = 2.07 \text{ moles of electrons}$$

The reduction of copper ions in solution occurs with the uptake of two electrons per ion. $Cu^{2+} + 2e^{-} \rightarrow Cu$, so every mole of electrons causes the deposition of half a mole of metallic copper. Hence the amount of copper deposited by 200,000 coulombs is

$$\frac{2.07 \text{ moles}}{2} = 1.035 \text{ moles of copper}$$

$$1.035 \times 63.54 \text{ g mole}^{-1} = 65.8 \text{ g of Cu.}$$

Problem 11.2. A conductivity cell had a resistance of 468 ohms when filled with 0.001 M HCl, a resistance of 1,650 ohms when filled with 0.001 M NaCl, and 1650 ohms when filled with 0.001M $NaNO_3$. The equivalent conductivity of $NaNO_3$ is 121. Calculate the specific conductance of 0.001 M $NaNO_3$ and the cell constant.

Solution.

$$\varkappa_{NaNO_3} = \Lambda_{NaNO_3} \times \frac{C}{1000}$$

$$\varkappa_{NaNO_3} = \frac{121 \times 0.001}{1000}$$

$$\varkappa_{NaNO_3} = 1.21 \times 10^{-4}$$

$$k \text{ (cell constant)} = \varkappa \times R$$

$$k \text{ (cell constant)} = 1.21 \times 10^{-4} \times 1650$$

$$k \text{ (cell constant)} = 0.2.$$

Problem 11.3. When a certain conductivity cell was filled with 0.020M KCl which has a conductivity of 0.2768 ohm^{-1} m^{-1}, it had a resistance of 82.40 ohm at 25°C as measured with a wheatstone bridge; when filled 0.0025M K_2SO_4, it had a resistance of 326.0 ohm. Calculate (*a*) the cell constant, (*b*) the conductivity of K_2SO_4 solution.

Solution.

$$\varkappa_{KCl} = C_{cell} \times 1/R$$

$$C_{cell} = \varkappa KCl \times R$$

$$C_{cell} = 0.2768 \text{ ohm}^{-1} \text{ m}^{-1} \times 82.40 \text{ ohm}$$

$$C_{cell} = 22.81 \text{ m}^{-1}.$$

$$\varkappa_{K_2SO_4} = C_{cell} \times 1/R$$

$$\kappa_{K_2SO_4} = 22.81\ \text{m}^{-1} \times \frac{1}{326\ \text{ohm}}$$

$$\kappa_{K_2SO_4} = 6.997 \times 10^{-2}\ \text{ohm}^{-1}\ \text{m}^{-1}.$$

Problem 11.4. The resistance of a decinormal solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 cm² in area was found to be 50 ohms. Calculate the equivalent conductance of the solution.

Solution. The equivalent conductance of the solution

$$\Lambda = \left(\frac{l}{a}\right) \times \frac{1}{R} \times \frac{1000}{C}$$

where $l = 1.80$ cm
$a = 5.40$ cm²
$R = 50$ ohms
$C = 0.1$ equiv.

Substituting the values of these parameters we get

$$\Lambda = \left(\frac{1.80}{5.40}\right) \times \frac{1}{50} \times \frac{1000}{0.1}$$
$$= 66.66\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}.$$

Problem 11.5. The equivalent conductivity of a normal solution at 18°C is 98.2 and for infinite dilution at the same temperature it was 131. Calculate the degree of ionisation of KCl at this dilution.

Solution. $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$

$\Lambda_v = 98.2$

$V_\infty = 131$

$$\alpha = \frac{98.2}{131} = 0.75$$

Problem 11.6. The conductivities at infinite dilution at 25°C of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 mhos respectively. If the equivalent conductance of $\frac{N}{100}$ solution of NH_4OH is 9.33 mhos, calculate the degree of NH_4OH at this dilution.

Solution. $\lambda_{o\,NH_4OH} = \lambda_{o\,NH_4Cl} + \lambda_{o\,NaOH} - \lambda_{o\,NaCl}$

$$= \lambda_{o\,NH_4^+} + \lambda_{o\,Cl^-} + \lambda_{o\,Na^+} + \lambda_{o\,OH^-} - \lambda_{o\,Na^+} - \lambda_{o\,Cl^-}$$

$$\lambda_{o\,NH_4OH} = 129.8 + 217.4 - 108.9$$

$$\lambda_{o\,NH_4OH} = 238.3\ \text{mhos}$$

$$\alpha = \frac{\lambda_{o\,NH_4OH}}{\lambda_{o\,NH_4OH}} = \frac{9.33}{238.3} = 0.0392 \text{ or } 3.92 \text{ per cent.}$$

Problem 11.7. The equivalent conductance of silver nitrate solution at 25°C for an infinite dilution was found to be 133.3 $ohm^{-1}\ cm^2\ equiv^{-1}$. The transport number of Ag^+ ions in very dilute solution of $AgNO_3$ is 0.464. Calculate the equivalent ionic conductances of Ag^+ and NO_3^- ions at infinite dilution.

Solution. Ionic conductance of

$$Ag^+, \lambda^o{}_{Ag^+} = 0.464 \times 133.3$$
$$= 61.9\ ohm^{-1}\ cm^2\ equiv^{-1}$$

Ionic conductance of

$$NO_3^-, \lambda^\circ{}_{NO_2^-} = 133.3 - 61.9$$
$$= 71.4\ ohm^{-1}\ cm^2\ equiv^{-1}.$$

Problem. 11.8. A 0.05 N solution of a salt occupying a volume between two platinum electrodes separated by a distance of 1.72 cm and having an area 4.5 sq.cm has a resistance of 250 ohms. Calculate the equivalent conductance of the solution.

Solution. Specific conductance, $\varkappa = \left(\frac{l}{a}\right)\frac{1}{R}$

$$\varkappa = \left(\frac{1.72}{4.5}\right)\frac{1}{250}$$
$$\varkappa = 1.528 \times 10^{-3}$$

Equivalent conductance, $\Lambda = \frac{\varkappa \times 100}{C}$

$$\Lambda = 1.528 \times 10^{-3} \times \frac{1000}{0.05}$$
$$\Lambda = 30.56\ ohm^{-1}\ cm^2\ equiv^{-1}.$$

Problem 11.9. The equivalent conductance Λ of an acqueous solution of 1.0283×10^{-3} g equivalent acetic per litre 48.15 $ohm^{-1}\ cm^2$ at 25°C; Λ_o is 390.7 $ohm^{-1}\ cm^2$. Calculate the degree of dissociation.

Solution. $\alpha = \frac{\Lambda}{\Lambda_o}$

$$\Lambda = 48.15\ ohm^{-1}\ cm^2$$
$$\Lambda_o = 390.7\ ohm^{-1}\ cm^2$$
$$\alpha = \frac{48.15\ ohm^{-1}\ cm^2}{390.7\ ohm^{-1}\ cm^2}$$
$$a = 0.1232.$$

Problem 11.10. A potential of 5.60 volts is applied between two electrodes placed 9.80 cm apart; how far would an NH_4^+ ion be expected to move in hour in a dilute solution of an ammonium salt at 25°C? The ionic conductance of NH_4^+ ion at 25°C is 73.4 $ohm^{-1}\ cm^2$.

Solution. Mobility of NH_4^+ ion $= \dfrac{73.4}{96{,}500}$

$$= 7.61 \times 10^{-4} \text{ cm sec}^{-1}.$$

$$\text{The potential gradient} = \frac{5.60}{9.80}$$

$$= 0.571 \text{ volt cm}^{-1}$$

$$\text{The actual velocity of } NH_4^+ \text{ ion} = 7.61 \times 10^{-4} \times 0.571$$

$$= 4.34 \times 10^{-4} \text{ cm sec}^{-1}$$

The distance moved by the ion in the solution in 1 hour

$$= 4.34 \times 10^{-4} \times 3600 \text{ cm.}$$

$$= 1.56 \text{ cm.}$$

Problem 11.11. In a Hittorf experiment aqueous silver nitrate solution was electrolysed between silver electrodes. The amount of silver nitrate in the anode compartment was 0.228 g before electrolysis and 0.2818 g after electrolysis. During the electrolysis 0.0194 g of copper was deposited on the cathode of a copper coulometer in series with the Hittorf cell. Calculate the transport numbers of the Ag^+ and NO_3^- ions.

Solution. The amount of Ag^+ in the anode compartment before electrolysis is

$$\frac{0.2278}{170} \text{ mole} = 1.340 \times 10^{-3} \text{ mole}$$

The amount of Ag^+ in the anode compartment after electrolysis is

$$\frac{0.2818}{100} = 1.658 \times 10^{-3} \text{ mole.}$$

The increase of Ag^+ during electrolysis is 0.318×10^{-3} mole. If no Ag^+ ions had migrated out of the anode compartment this increase would have been

$$\frac{0.0194}{31.75} \text{ mole} = 0.611 \times 10^{-3} \text{ mole}$$

∴ The amount of Ag^+ which has migrated is $(0.611-0.318) \times 10^{-3}$ mole $= 0.293 \times 10^{-3}$ mole.

Transport number of silver ions, $t_{Ag^+} = \dfrac{0.293 \times 10^{-3}}{0.611 \times 10^{-3}} = 0.480.$

Transport number of nitrate ions, $t_{NO_3^-} = 1 - 0.480 = 0.520.$

Problem 11.12. The speed ratio of the silver and nitrate ions in a solution of $AgNO_3$ electrolysed between silver electrodes is 0.916. Calculate the transport number of the two ions.

Solution. $$\frac{\text{Speed of cation}}{\text{Speed of anion}} = \frac{\text{Fall around anode}}{\text{Fall around cathode}} = \frac{1-t_-}{t_-}$$

where t_- is the transport number of the anion.

$$\frac{1-t_-}{t_-} = 0.916$$

$$1-t_- = 0.916\, t_-$$

$$t_- = 0.521$$

$$t_+ = 1-t_- = 1-0.521$$

$$t_+ = 0.479.$$

Hence the transport number of the anion and cation are 0.521 and 0.479 respectively.

Problem 11.13. For a saturated solution of AgCl at 25°C, $\varkappa$ for water used for preparing the solution was 1.60×10^{-6} ohm^{-1} cm^{-1}. Determine the solubility of AgCl in water, in moles per litre at 25°C.

$$\Lambda_{\circ\,AgCl} = 138.3 \text{ ohm}^{-1} \text{ cm}^{-1}.$$

Solution. $$\varkappa_{AgCl} = \varkappa_{AgCl\ (\text{saturated solution})} - \varkappa_{\text{water}}$$

$$\varkappa_{AgCl} = (3.41-1.60)\, 10^{-6}$$

$$\varkappa_{AgCl} = 1.81 \times 10^{-6}$$

$$\Lambda_\circ = 1000\, \frac{\varkappa}{S}$$

$$S = 1000\, \frac{\varkappa}{\Lambda_\circ}$$

$$S = \frac{1000 \times 1.81 \times 10^{-6}}{138.3}$$

$$S = 1.31 \times 10^{-5} \text{ g equivalent litre}^{-1}.$$

Problem 11.14. Hittorf cell contains 0.1 *M* $CuSO_4$ solution and has copper electrodes. After passage of certain quantity of electricity, it is found that the anode solution gains 0.006 mole of $CuSO_4$, but that the total weight of the anode compartment had not changed in weight. Calculate the number of Faradays passed through the cell and the transport number of SO_4^{2-} ion.

Solution. The reaction occurring at the anode on passing one Faradary, is,

$$\tfrac{1}{2}\, Cu \rightleftharpoons \tfrac{1}{2}\, Cu^{2+} + e^-$$

On the passage of electricity, the anode compartment loses t_+ equivalent of Cu^{2+} and gains t- equivalents of SO_4^{2-}; the net change in the compartment is then gain of t_- equivalents of $CuSO_4$. However, if the anode plus anode compartment is weighed the only change in weight that occurs is due to the loss of Cu^{2+} and the gain of t_-, SO_4^{2-} ions. Since there is no change in weight, we have,

$$t_+\left(\frac{63.5}{2}\right) = t_-\left(\frac{96}{2}\right)$$

from which $t_+ = 0.60$ and $t_- = 0.40$. The net gain of 0.006 mole or 0.012 equivalents of $CuSO_4$ than corresponds to $0.012/0.40 = 0.030$ faraday.

Problem 11.15. In a moving boundary experiment with 0.100 N KCl, using 0.065N LiCl as indicator solution, a constant current of 0.005893 ampere was passed for 2130 sec and the boundary was observed to move through 5.60 cm in a tube of 0.1142 sq. cm cross section. Calculate the transference numbers of K^+ and Cl^- ions.

Solution. $t_+ = \dfrac{l \times a \times F \times c}{Q}$

$$Q = 0.005893 \times 2130 \text{ coulombs}$$
$$c = 10^{-4} \text{ g equivalent per c.c.}$$
$$l = 5.6 \text{ cm}$$
$$a = 0.1142 \text{ sq. cm}$$
$$t_+ = \frac{5.60 \times 0.1142 \times 96{,}500 \times 10^{-4}}{0.005893 \times 2130}$$
$$t_+ = 0.492$$
$$t_- = 0.508.$$

Hence the transference numbers of K^+ and Cl^- are 0.492 and 0.508 respectively.

EXERCISES

11.1. A Cu^{2+} solution is electrolysed using a current of 3.0 amp. What weight of copper will be deposited in 30 minutes? [Ans. 1.78 g.]

11.2. In the electrolysis of a $CuSO_4$ solution what volume of oxygen at STP is liberated at the anode in the time that it takes to deposit 5.08 g of Cu on the cathode? [Ans. 0.896 litre.]

11.3. Ten amperes of current flowed for one hour through water containing little sulphuric acid. How many litres of gas were formed at both electrodes at 27°C and 740 mm pressure? [Ans. 7.08 litres.]

11.4. A current of 0.5 ampere is passed through alkaline aqueous solution for one hour. What volume of hydrogen will be evolved at 17°C and 750 mm pressure? Given that one coulomb of electricity deposits 0.001118 g of silver. [Ans. 234.6 c.c.]

11.5. An electric current is passed through three cells connected in series containing respectively solutions of $CuSO_4$, $AgNO_3$ and KI. What weight of

Ag and I_2 will be liberated when 1.25 g of Cu gets deposited?

[**Ans.** Ag = 4.28 g, I_2 = 5.00 g.]

11.6. The equivalent conductance of 0.100N solution of $MgCl_2$ is 97.1 cm²/ohm equivalent at 25°C. A cell with electrodes that are 1.50 cm² in surface area and 0.50 cm apart is filled with 0.100N $MgCl_2$. How much current will flow when the potential difference between the electrodes is 5.00 V?

[**Ans.** 0.146 amp.]

11.7. Given the following Λ_0 values at 25°C in cm²/ohm equivalent; $AgNO_3$. 133.4, KCl 149.9; KNO_3 144.9 (*a*) What is the equivalent conductance at infinite dilution of AgCl? (*b*) Silver chloride is only slightly soluble in water, and a saturated solution of AgCl may be regarded as infinitely dilute. At 25°C, the specific concuctance *K*, of a saturated solution is 1.80×10^{-6} ohm^{-1} cm^{-1} after correction for the conductance of pure water. What is the solubility of AgCl in moles per litre at 25°C?

[**Ans.** (*a*) 138.4 cm² ohm^{-1} $equivalent^{-1}$, (*b*) 1.30×10^{-5}M.]

11.8. At 25°C the resistance of a cell filled with 0.01 demal KCl solution is 255 ohms. The resistance of the same cell filled with 0.1N NH_4OH is 2030 ohms. What is the degree of dissociation of NH_4OH in this solution?

[**Ans.** α=0.0134.]

11.9. A conductivity cell filled with 0.01 demal KCl solution gives at 0°C a resistance of 11,210 ohms. The distance between the electrodes in the cell is 6 cm. Calculate (*a*) the cell constant, and (*b*) the average cross-sectional area of the electrodes. [**Ans.** (*a*) 8.673, (*b*) 0.069.]

11.10. At 25°C the equivalent conductance of propionic acid at infinite dilution is 386.6 cm² $equiv^{-1}$ ohm^{-1}, and the ionization constant is 1.43×10^{-5}. Calculate the equivalent conductance of a 0.05N solution of propionic acid at 25°C. [**Ans.** 632 cm² $equiv^{-1}$ ohm^{-1}.]

11.11. The specific conductance at 25°C of a saturated aqueous solution of $SrSO_4$ is 1.482×10^{-4}, while that of water used is 1.5×10^{-6} mho cm^{-1}. Determine at 25°C the solubility in grams per litre of $SrSO_4$ in water.

[**Ans.** 0.0967 g/litre.]

11.12. The resistance of a conductivity cell is 220,000 Ω when it is filled with water, 100 Ω when filled with 0.02 M KCl, and 102,000 Ω when filled with water saturated with AgCl. The equivalent conductivity of AgCl is calculated to be 126.8 at 25°C, whereas that for KCl is known to be 138.3. Assume that the solutions are prepared with water of the same resistance as given above. Calculate (*a*) the cell constant, (*b*) the specific conductivity of the saturated solution of AgCl. Neglect the variation of equivalent conductivity with concentration. [**Ans.** (*a*) 0.277, (*b*) 2.71×10^{-6}.]

11.13. When a solution of specific conductance 1.342×10^{-2} ohm^{-1} cm^{-1} was placed in a cell with parallel electrodes, the resistance was found to be 170.5 ohms. The area of the electrodes was 1.86 sq. cm. Determine the distance between the electrodes and the cell constant.

[**Ans.** 4.254 cm, 2.88.]

11.14. A conductivity cell having a resistance of 9950 ohms with N/10 acetic acid at 25°C, had a resistance of 3735 ohms with N/100 KCl at 25°C. The specific resistance of N/100 KCl at 25°C is 721 ohms. Calculate the specific conductance and equivalent conductance of acetic acid.

[**Ans.** $\kappa=5.77\times10^{-4}$ ohm^{-1} cm^{-1}, Λ=5.77 cm² ohm^{-1} $equiv^{-1}$.]

11.15. A N/50 solution of a weak acid has a specific conductivity of 3.129×10^{-4} mhos. The degree of dissociation of the acid is 0.0447. Calculate the value of equivalent conductivity at infinite dilution.

[Ans. 35 cm^2 ohm^{-1} $equiv^{-1}$.]

11.16. The equivalent conductance of N/32 solution of a weak acid is 9.2 ohm^{-1} cm^2 $equiv^{-1}$. If the equivalent conductance of this acid at infinite dilution is 385 ohm^{-1} cm^2 $equiv^{-1}$, what is the dissociation constant of the acid?

[Ans. 1.88×10^{-5} mole $litre^{-1}$.]

11.17. In a conductance cell, the resistance of a 5×10^{-4} mole dm^{-3} aqueous solution of potassium chloride and a sample of water with which this solution was made are 6.13×10^4 ohms and 8.0×10^6 ohms respectively at 25°C. Calculate the molar conductivity of 5×10^{-4} mole dm^{-3} aqueous potassium chloride at this temperature. The cell constant of this cell is 456.5 m^{-1}. [Ans. 1.478×10^{-2} ohm^{-1} m^2 $mole^{-1}$.]

11.18. The limiting molar conductivities of aqueous ammonium chloride, sodium chloride and sodium hydroxide are 1.497×10^{-2}, 1.2645×10^{-2} and 2.478×10^{-2} ohm^{-1} m^2 $mole^{-1}$ respectively at 25°C Calculate the limiting molar conductivity of aqueous ammonia at this temperature.

[Ans. 2.7105×10^{-2} ohm^{-1} m^2 $mole^{-1}$.]

11.19. The limiting molar conductivity of aqueous sodium chloride is 1.089×10^{-2} ohm^{-1} m^2 $mole^{-1}$ at 18°C and the transport number of the sodium ions in this electrolyte is 0.395. Calculate the limiting mobilities of sodium and chloride ions at this temperature.

[Ans. Ionic mobility of $Na^+ = 4.46 \times 10^{-8}$ $m^2 s^{-1}$ v^{-1} ionic mobility of $Cl^- = 6.83 \times 10^{-8}$ m^2 s^{-1} v^{-1}.]

11.20. To determine the cell constant of a conductivity cell, a student fills the cell with a 0.0100M KCl solution and measures the resistance of cell to be 635.2 ohms. What is the cell constant for the cell? [Ans. 0.01114 m.]

11.21. Kohlrausch found from conductivity measurements on very pure water that the degree of dissociation of water is $\alpha = 1.9 \times 10^{-9}$. Determine the molar conductance and the conductivity of water at this temperature.

[Ans. $\Lambda = 1.04 \times 10^{-10}$ ohm^{-1} m^2 $mole^{-1}$, $K = 5.77 \times 10^{-6}$ ohm^{-1} m^{-1}.]

11.22. At 18°C the conductivities at infinite dilution of NH_4Cl, NaOH, NaCl are 129.8, 217.4 and 108.9 mhos respectively. If the equivalent conductivity of N/100 solution of NH_4OH is 9.33 mhos, calculate the degree of dissociation of NH_4OH at this dilution. [Ans. 3.92 per cent]

11.23. The specific conductance of a solution of a weak acid is 2.1×10^{-4} mho. At the same temperature the ionic conductances of the two ions are 349 and 76 ohm^{-1} cm^2 respectively. Calculate the degree of dissociation of the acid in the above solution of N/10 concentration. [Ans. 4.97×10^{-3}.]

11.24. The molar conductivity at infinite dilution of $AgNO_3$, NaCl and $NaNO_3$ is 116.5, 110.3 and 105.2 mhos respectively. The specific conductivity of AgCl in water is 2.40×10^{-6} mhos, and of water used in the experiment is 1.6×10^{-6} mho. Calculate the solubility of AgCl.

[Ans. 1.462×10^{-3} g/litre.]

11.25. A conductance cell with a constant of 2485 cm^{-1} is filled with a 0.1N KCl solution for which $\Lambda = 141.3$ ohm^{-1} cm^2 at 25°C. If the specific conductance of the water is 1.0×10^{-6} ohm^{-1} cm^{-1}, what is the resistance of the solution? [Ans. 2150 ohms.]

11.26. When water with a specific conductance of 1.12×10^{-6} ohm^{-1} cm^{-1} was saturated at 25°C with barium sulphate the value of specific conductance increased to 4.63×10^{-6} ohm^{-1} cm^{-1}. Calculate the solubility of barium sulphate at that temperature. [**Ans.** 2.85 mg/litre.]

11.27. A 4.00 molal solution of MCl_3 was electrolysed between platinum electrodes. After electrolysis, the cathode portion in the Hittorf apparatus was 3.15 molal in MCl_3 and 1.00 molal in MCl_2. What was the transference number of M^{3+}? [**Ans.** $t_{M^{3+}}=0.45$, $t_{Cl^-}=0.55$.]

11.28. A certain volume of the anode solution contained 13.1426 g and 1.25533 g of silver at the beginning and at the end of the transport experiment. The weight of silver deposited at the cathode during the experiment was 1.2591 g. Calculate the transport number of silver and nitrate ion.

[**Ans.** $t_{Ag^+}=0.468$, $t_{NO_3}=3.532$.]

11.29. A dilute solution of copper sulphate was electrolysed using platinum electrodes. The amount of copper per unit weight of the anodic solution was found to be 0.6350 g and 0.6236 g, before and after electrolysis respectively. The weight of silver deposited in a silver coulometer placed in series was found to be 0.1351 g. Calculate the transport numbers of Cu^{2+} and SO_4^{2-} ion. The atomic weight of Ag=107.88 and of Cu=63.6.

11.30. A 4.00 molal solution of MCl_3 was electrolysed between platinum electrodes. After electrolysis, the cathode portion in the Hittorf apparatus was 3.15 molal in MCl_3 and 1.00 molal in MCl_2. What was the transport number of M^{3+}? [**Ans.** 0.45.]

11.31. A solution containing 3.654 g of KCl per 100 g electrolysed using a cathode consisting of Ag coated with AgCl. By passing current which deposits 1.978 g of silver in a coulometer 122.93 g of cathode solution was found to contain 5.136 g KCl. Calculate the transference number of K^+ ions.

[**Ans.** 0.735.]

11.32. A solution of silver nitrate containing 1.139 mg of silver per g of solution was electrolysed between silver eletrodes and the anode liquid after electrolysis contained 39.66 mg of silver in 20.09 g of solution. In a silver voltameter in series with electrolytic cell 32.10 mg of silver got deposited. Calculate the transport numbers of silver and nitrate ions.

[**Ans.** $t_{Ag^+}=0.48$, $t_{NO_3^-}=0.52$.]

11.33. The speed ratio of silver and nitrate ions in a solution of silver nitrate electrolysed between silver electrodes is 0.916. Find the transport number of ions. [**Ans.** $t_{Ag^+}=0.478$, $t_{NO_3^-}=0.522$.]

11.34. A silver nitrate solution containing 0.00739 g of $AgNO_3$ per gram of H_2O is electrolysed between silver electrodes. During the experiment 0.078 g of Ag was deposited at the cathode. At the end of the experiment the anode portion contains 23.14 g of H_2O and 0.236 g of $AgNO_3$. What are the transport numbers of Ag^+ and NO_3^-? [**Ans.** $t_{Ag^+}=0.47$, $t_{NO_3^-}=0.53$.]

11.35. A solution of hydrochloric acid was electrolysed in a transference cell between platinum electrodes. The cathode compartment contained 0.177 g of chloride ions before the electrolysis and 0.163 g afterwards. A silver coulometer in a series had a deposit of silver equivalent to 0.0825 g of chloride ions. What are the transference numbers of H^+ and Cl^- ions?

[**Ans.** $t_{H^+}=0.830$, $t_{Cl^-}=0.170$.]

11.36. In an experiment, $AgNO_3$ solution was electrolysed between silver electrodes. The silver ions in the anode compartment increased by 0.030563 g equivalent. The silver deposited in a voltameter placed in the circuit was 0.114 g. Calculate the transport number of silver ions (at. wt. of $Ag=108$).
[**Ans.** 0.467.]

11.37. A moving boundary experiment is carried out with a 0.1N solution of hydrochloric acid at 25°C ($\varkappa=0.0424$ ohm^{-1} cm^{-1}). Sodium ions are caused to follow the hydrogen ions. A current of three milliamperes is passed through the tube of 0.3 cm^2 cross-sectional area, and it is observed that the boundary moves 3.08 cm in 1 hour. Calculate (*a*) the hydrogen ion mobility, (*b*) the hydrogen ion transference number, and (*c*) the chloride ion mobility.
[**Ans.** (*a*) 3.36×10^{-5} cm^2 $volt^{-1}$ sec^{-1}, (*b*) 0.826, (*c*) 76.6×10^{-5} cm^2 $volt^{-1}$ sec^{-1}.]

11.38. The transport number of Ag^+ ions is $AgNO_3$ is 0.48. The equivalent conductivity of $AgNO_3$ at infinite dilution is 120 mhos. Calculate the ionic mobility and absolute velocities of two ions.
[**Ans.** Ionic mobilities: $Ag^+=57.6$ mhos; $NO_3^-=62.4$ mhos. Absolute velocities cm sec^{-1}: $Ag^+=5.97\times10^{-4}$ $NO_3^-=6.32\times10^{-4}$.]

11.39. In a moving boundary experiment with 0.02N NaCl using an autogenic rising boundary from a cadmium anode, a current of 0.0016001 ampere was passed through the solution in a tube of 0.1115 cm^2 cross-section. The time taken for the boundary to move various distances was as follows:

Distance (*c*)	0	1.00	3.00	6.00	8.00	10.00
Time (sec)	0	344	1036	2070	2757	3454

[**Ans.** 0.3893.]

11.40. In a moving boundary experiment, the boundary between a 0.0998N solution of calcium chloride and a lithium chloride solution swept through a volume of 1.11 cm^3 in 4406 sec, using a current of 5.594×10^{-3} amp. Calculate the transport number of Ca^{2+} ion. [**Ans.** 0.4341.]

11.41. The transference number of Na^+ in dilute NaCl solution is 0.4 and $\lambda_{Cl^-}=75$. The following resistances have also been measured for a conductivity cell filled successively with indicated solution 0.1M KCl solution, 7000 ohms, a solution 0.1M in KCl and 0.2M in NaCl 2600 ohms. Calculate Λ KCl from the above data. [**Ans.** 147 ohm^{-1} cm^2.]

11.42. Solution Aconsists of 50 ml of 0.02M NaOH and solution *B* of 50 ml of 0.0446M HCl. The λ values for H^+, Na^+, OH^- and Cl^- are 350, 50, 200 and 75 respectively. The two solutions are now mixed. Calculate the transference number of Na^+ in the mixture and also the specific conductance of the mixture. [**Ans.** $t_{Na^+}=0.0725$, $\varkappa=6.9\times10^{-3}$.]

11.43. Calculate the velocity of Li^+ ions in 0.1M LiCl, when a current of one ampere is passed through a column of the solution. The cross-sectional area of the column is 2 cm^2, and the equivalent conductivities of Li^+ and Cl^- ions are 40 and 75 respectively. [**Ans.** 1.8×10^{-2} cm/sec.]

12

IONIC EQUILIBRIUM

INTRODUCTION

In a solution of any electrolyte there should be an equilibrium between the free ions, and undissociated molecules. There exists following equilibria,

$$MA \rightleftharpoons M^+ + A^-$$

the equilibrium constant is

$$K = \frac{a_{M^+} \times a_{A^-}}{a_{MA}} \qquad \ldots (1)$$

For weak electrolytes, the ionic concentrations are low and the solutions do not deviate appreciably from ideal behaviour. The activities can, therefore, be replaced by concentration. Equation (1) can therefore be written as,

$$K_c = \frac{\alpha^2 C}{(1-\alpha)} \qquad \ldots (2)$$

where C is the concentration in moles per litre and α is the degree of dissociation. Since $V = \frac{1}{C}$, the volume in litres occupied by 1 g mole of the electrolyte, we have,

$$K_c = \frac{\alpha^2}{(1-\alpha)\,V} \qquad \ldots (3)$$

This equation representing the variation of degree of dissociation with dilution is known as the Ostwald's Dilution Law.

The pH. The pH of a solution is defined as the negative logarithm to the base 10 of the hydrogen ion concentration in gram ions per litre. Thus

$$\text{pH} = -\log\,[H^+] \qquad \ldots (4)$$

In an aqueous solution, the ionic product of water is expressed as,

$$a_{H^+} \cdot a_{HO^-} = K_w = 10^{-14} \qquad \ldots (5)$$

In homogeneous reactions, all components are in a single phase, i.e., all reactants and products are either in solution or in the gaseous state. The reactions in which all the components are not in a single phase are called heterogeneous reactions. For example, in a saturated silver chloride solution containing some solid AgCl, the equilibrium is,

$$AgCl(s) \rightleftharpoons Ag^+ \text{ (in solution)} + Cl^- \text{ (in solution)}$$

For this reaction the equilibrium expression is

$$K_{eq} = \frac{[Ag^+]\,[Cl^-]}{[AgCl\ (s)]} \qquad \ldots (6)$$

Equation (6) can be written as

$$[Ag^+]\,[Cl^-] = K_{eq}.\,[AgCl\ (s)] \qquad \ldots (7)$$

Since the concentration of [AgCl (s)] is constant, we can write,

$$[Ag^+]\,[Cl^-] = K_{sp} \qquad \ldots (8)$$

K_{sp} is called the solubility product constant. The insoluble salt MA will precipitate from solution whenever $[M^+]\,[A^-]$ exceeds K_{sp}. If the solubility product constant and the concentration of one of the ions is known, the concentration of the other ion in solution may be calculated. Addition of a common ion will change the position of the solubility equilibrium. Thus addition of Cl^- will shift the following reaction to the left.

$$AgCl\ (s) \rightleftharpoons Ag^+ + Cl^-$$

If K_{sp} is known, then the quantitative aspects of the shift in the equilibrium may be calculated.

Hydrolysis: When salts of a strong base and a strong acid are added to water, the hydrogen ions concentration remains unchanged. However, when salt formed from strong acids and weak bases or salts formed from weak acids and strong bases are added to water, the hydrogen ion concentration changes because of a reaction between the ions salt and water. The reaction is called hydrolysis.

Hydrolysis of a salt of weak acid and strong base. Consider the hydrolysis of a salt BA formed by combination of a weak acid HA and a strong base BOH. Here the hydrolysis will be due to the anion of the acid and is represented as,

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad \ldots (9)$$

From the law of Mass Action,

$$K_h = \frac{a_{HA} \cdot a_{OH^-}}{a_{A^-}} \qquad \ldots (10)$$

The constant K_h, known as the hydrolytic constant of A^-, determines the extent to which the ion A^- will undergo hydrolysis

$$K_h = \frac{K_w}{K_a} \qquad \ldots (11)$$

where K_a is the ionization constant of the acid and K_w is the ionic product of water.

Hydrolysis of a salt of strong acids and weak bases. In salts of this category the cation B^+ of the weak base will suffer hydrolysis according to the reaction,

$$B^+ + H_2O = BOH + H^+ \qquad \ldots (12)$$

The hydrolytic constant K_h will be given by

$$K_h = \frac{K_w}{K_b}. \qquad \ldots (13)$$

where K_b is ionization constant of the base.

Hydrolysis of a salt of weak acids and weak bases. In this case the salt BA is the product of the interaction of a weak acid HA and a weak base BOH, such as ammonium acetate. Both the cation and the anion of the salt undergo hydrolysis according to the reaction,

$$B^+ + A^- + H_2O = BOH + HA \qquad \ldots (14)$$

The hydrolytic constant K_h is given by

$$K_h = \frac{K_w}{K_a K_b} \qquad \ldots (15)$$

Buffer solutions. Solutions composed of an acid and one of its salts or of a base and one of its salts, possess the ability to resist to a greater or lesser degree changes, in pH when some acid or base is added to them. Such solutions, which resist changes in pH when acids or bases are added, are called buffer solutions. Buffers are used whenever solutions of known pH are required or whenever it is necessary to keep the pH of a solution constant. The pH change of a buffer solution is given by the relation,

$$pH \simeq pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \qquad \ldots (16)$$

pH indicators. Indicators are used to detect the equivalence point in titration of solutions of unknown strengths with a standard solution, i.e., a solution whose strength is exactly known. In acidimetric titration a hydrogen ion indicator is used. This indicator is a substance which in certain limits changes colour as the pH of the solution changes during the titration of an acid with a base. Let HI_n represent the unionized form of an indicator which is a weak acid. It ionizes as,

$$HI_n + H_2O \rightleftharpoons H_3O^+ + I_n^-. \qquad \ldots (17)$$

The unionized molecule HI_n differs in colour from its conjugate base I_n^-.

$$K_{I_n} = \frac{[H_3O^+][I_n^-]}{[HI_n]} \qquad \ldots (18)$$

where K_{I_n} is known as indicator constant and the various terms in brackets stand for the concentration of the respective species

$$\mathrm{pH} = \mathrm{p}K_{I_n} + \log \frac{[I_n^-]}{[\mathrm{H}_{I_n}]} \qquad \ldots (19)$$

$pK_{I_n} = -\log K_{I_n}$ is known as indicator exponent

$$\mathrm{pH} = pK_{I_n} \pm 1 \qquad \ldots (20)$$

The indicator is between these two extremes. This is known as useful indicator range.

Problem 12.1. Calculate the pH of a 0.56 mole dm^{-3} aqueous solution of potassium hydroxide assuming ideal behaviour.

Solution. A 0.56 mole dm^{-3} solution of K^+OH^- will contain 0.56 mole dm^{-3} of OH^-

$\therefore$ $[OH^-] = 5.6 \times 10^{-1}$ mole dm^{-3}

Hence

$$\begin{aligned}
pOH &= -\log [OH^-] \\
pOH &= -\log (5\cdot 6 + 10^{-1}) \\
pOH &= -\log (\bar{1}.75) \\
pOH &= -(-1+0.75) \\
pOH &= -(-0.25) \\
pOH &= 0.25 \\
pH + pOH &= 14 \\
pH &= 14 - 0.25 \\
pH &= 13.75.
\end{aligned}$$

Problem 12.2. Find the pH of a 1.00×10^{-7} molar solution of HCl. The ionic product of water is 10^{-14}.

Solution. Since $[H^+][OH^-] = 1.00 \times 10^{-14}$ ... (1)

A mass balance on chloride ion combined with the charge balance gives the proton condition,

$$[OH^-] = [H^+] - 1.00 \times 10^{-7} \qquad \ldots (2)$$

Since the solution is so dilute, $[OH^-]$ is not negligible compared to 1.00×10^{-7} and the equations must, therefore, be solved exactly. Substitute the value of $[OH^-]$ from Equation (2) in (1) we get

$$[H^+]^2 - 1.00 \times 10^{-7} [H^+] - 1.00 \times 10^{-14} = 0 \qquad \ldots (3)$$

On solving Equation (3) for the positive root we get

$$[H^+] = 1.62 \times 10^{-7}$$

$$pH = 6.79.$$

Problem 12.3. What is the pH value of a solution in which $[H_3O^+] = 3.0 \times 10^{-3}$ g ion/*l*?

Solution. $pH = \log \dfrac{1}{[H_3O^+]} = \log \dfrac{1}{3 \times 10^{-3}} = \log\left(\dfrac{10^3}{3}\right)$

$$pH = 3 - 0.48 = 2.52$$

$$pH = 2.52.$$

Problem 12.4. Calculate (*i*) the $[H_3O^+]$, and (*ii*) $]OH^-]$ of a solution that has a pH value of 6.5.

Solution. (*i*) $[H_3O^+]=10^{-pH}$

$$[H_2O^+]=10^{-6.5}$$

$$[H_3O^+]=10^{-7}\times 10^{0.5}$$

$$[H_3O^+]=3\times 10^{-7} \text{ g ion}/l$$

(*ii*) $10^{0.5}$=Number whose log is 0.5=3

Since $[H_3O^+]\,[OH^-]=1\times 10^{-14}$

$$[OH^-]=\frac{1\times 10^{-14}}{3\times 10^{-7}}=3\times 10^{-8}$$

$$[OH^-]=3.0\times 10^{-8} \text{ g ion}/l.$$

Problem 12.5. Find (*a*) $[H_3O^+]$, and (*b*) percentage ionization of 0.2M acetic acid solution. The ionization constant of acetic acid is 1.8×10^{-5}.

Solution. Acetic acid ionizes as,

$$CH_3COOH+H_2O\rightleftharpoons CH_3COO^-+H_3O^+$$

$$K_{\text{ionization}}=\frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

Concentration of acetic acid is 0.2 mole/*l*. Let $x=[H_3O^+]$ then

$$0.2-x=[CH_3COOH]$$

$$\therefore \quad 1.8\times 10^{-5}=\frac{x\times x}{0.2-x}$$

$$x=1.9\times 10^{-3}$$

$$[H_3O^+]=1.9\times 10^{-3} \text{ g ion}/l$$

Let y be the fraction of acetic acid ionized,

$$0.2\,y=1.9\times 10^{-3}$$

$$y=\frac{1.9\times 10^{-3}}{0.2}=9.5\times 10^{-3}=0.0095$$

or 0.95 per cent.

Problem 12.6. An indicator is a weak acid and the pH range of its colour change is 3.1 to 4.5. if the neutral point of the indicator is in the centre of this pH range, calculate the ionization constant of the indicator.

Solution. The centre of the range may not be calculated by averaging the pH values, since pHs are exponential in form. The centre of the range can be determined by averaging the corresponding concentrations of H^+.

$$pH=3.1$$

$$\log\,[H^+]=-3.1=0.9-4.0$$

$$[H^+]=7.9\times10^{-4}=79.0\times10^{-5}$$
$$pH=4.5$$
$$\log[H^+]=-4.5=0.5-5$$
$$[H^+]=3.2\times10^{-5}$$
$$\text{Average }[H^+]=\frac{79.0\times10^{-5}+3.2\times10^{-5}}{2}$$
$$=4.1\times10^{-4}$$
$$\text{where }[H^+]=4.1\times10^{-4}\text{ M, }K=[H^+]$$
$$\therefore\quad K=4.1\times10^{-4}$$

Problem 12.7. What is the pH of a solution for which $[OH^-]=0.15M$?

Solution. $[OH^-]=1.5\times10^{-1}$

$$\log[OH^-]=\log1.5+\log10^{-1}$$
$$=0.2-1$$
$$=-0.8$$
$$pOH=0.8$$
$$pH=14-0.8$$
$$=13.2.$$

Problem 12.8. What is the $[H^+]$ of a solution with a pH of 10.6?

Solution. $pH=-\log[H^+]=10.6$

$$\log[H^+]=-10.6$$
$$=0.4-11$$
$$=\text{antilog }0.4\times10\text{ antilog }(-11)$$
$$[H^+]=2.5\times10^{-11}$$

Problem 12.9. To 10 cm^3 of 0.1 mole dm^{-3} HCl was added 9.6 cm^3 of 0.1 mole dm^{-3} NaOH. Calculate the pH of the final solution.

Solution. Since 9.6 cm^3 of 0.1 mole dm^{-3} NaOH will completely neutralize an equivalent quantity of the strong acid, HCl.

$$HCl+(Na^+)OH^-\rightarrow H_2O+(Na^+)Cl^-$$

Since 10 cm^3 of 0.1 mole dm^{-3} HCl was initially present, a quantity equivalent to 0.4 cm^3 of 0.1 mole dm^{-3} HCl will remain unneutralized in the solution whose total volume is now 19.6 cm^3.

$\therefore$ Concentration of HCl remaining neutralized

$$=0.4/19.61\times0.1\text{ mole dm}^{-3}$$
$$=2.04\times10^{-3}\text{ mole dm}^{-3}$$

$[H^+]$ in 1 mole dm^{-3} HCl$=1$ mole dm^{-3}

$\therefore$ $[H^+]$ in 2.04×10^{-3} mole dm^{-3} HCl

$$=2.04\times10^{-3}\text{ mole dm}^{-3}$$
$$pH=-\log[H^+]=-\log(2.04\times10^{-3})$$

$$pH = -3.31 = -(-3+0.31)$$
$$pH = 2.69.$$

Problem. 12.10. A solution is made 1.00×10^{-3} M in Ag^+ by adding enough water to 1.00×10^{-3} moles of $AgNO_3$ to make 1 litre of solution. Will any AgCl precipitate if 10.0×10^{-4} moles of NaCl is added? K_{sp} for AgCl is 2.8×10^{-10} mole²/l².

Solution. Silver chloride (AgCl) will precipitate provided the product $[Ag^+][Cl^-]$ exceeds 2.8×10^{-10} mole²/l², AgCl precipitates.

$$[Ag^+] = 1.00 \times 10^{-3} \text{ M}; [Cl^-] = 1.00 \times 10^{-4} \text{ M}$$

The product of these two quantities (1.00×10^{-7} mole²/l²) is much larger than 2.8×10^{-10} mole²/l². Therefore some AgCl must precipitate until the condition

$$[Ag^+][Cl^-] = 2.8 \times 10^{-10} \text{ mole}^2/\text{l}^2 \text{ is reached.}$$

Problem 12.11. A solution is 0.010 M in cuprous ion (Cu^+) and 0.0010 M in lead ion (Pb^{2+}). Chloride ion is slowly added. Will $PbCl_2$ ($K_{sp} = 1.6 \times 10^{-5}$ mole³/l³) or CuCl ($K_{sp} = 3.2 \times 10^{-7}$ mole²/l²) precipitate first? Show why.

Solution. The ionic reactions occurring in the solution are

$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$$
$$CuCl \rightleftharpoons Cu^+ + Cl^-$$

lead chloride precipitates when

$$[Pb^{2+}][Cl^-]^2 = K_{sp} = 1.6 \times 10^{-5} \text{ mole}^3/\text{l}^3$$

In this case

$$[Pb^{2+}] = 0.0010 \text{ M}$$

Therefore, $PbCl_2$ precipitates when

$$[Cl^-] = \sqrt{\frac{1.6 \times 10^{-5}}{0.00100}} = 1.3 \times 10^{-1} \text{ M}$$

Cuprous chloride precipitates when

$$[Cu^{2+}][Cl^-] = 3.2 \times 10^{-7} \text{ mole}^2/\text{l}^2$$

In this case,

$$[Cu^+] = 0.010 \text{ M}$$

Therefore, CuCl precipitates when

$$[Cl^-] = \frac{3.2 \times 10^{-7}}{0.010} = 3.2 \times 10^{-5} \text{ M}$$

It is obvious therefore that CuCl would precipitate first as $[Cl^-]$ of 3.2×10^{-5} M is reached earlier than $[Cl^-]$ of 1.3×10^{-1} M of $PbCl_2$.

Problem 12.12. Calculate the solubility of thallous chloride at 20°C from its K_s, 1.7×10^{-4}.

Solution. Thallous chloride undergoes dissociation as under:

$$TlCl\ (s) \rightleftharpoons Tl^+ + Cl^-$$

$$K_S = [Tl^+]\ [Cl^-] = 1.7 \times 10^{-4}$$

The solubility of $TlCl = C$

$$[Tl^+] = [Cl^-] = C$$

$$C^2 = 1.7 \times 10^{-4}$$

$$C = \sqrt{1.7 \times 10^{-4}} = 1.3 \times 10^{-2} \text{ mole/litre}$$

Problem 12.13. The average of several determinations of the solubility of silver chloride in water at 25°C was 0.00194 g/litre. Calculate the pK_S of AgCl by using this value.

Solution. $AgCl\ (s) \rightleftharpoons Ag^+ + Cl^-$

$$K_S = [Ag^+]\ [Cl^-]$$

$$[Ag^+] = [Cl^-] = C$$

$$AgCl = 107.87 + 35.453 = 143.323$$

$$= \frac{35.453}{143.323} \text{ g/mol}$$

$$C = \frac{1.94 \times 10^{-3}}{1.43 \times 10^{-2}} = 1.36 \times 10^{-5} \text{ mole/litre}$$

$$K_S = (1.36 \times 10^{-5})^2 = 1.85 \times 10^{-10}$$

$$pK_S = -\log K_S = -\log\ (1.85 \times 10^{-10})$$

$$pK_a = -[0.27 + (-10.00)] = -(-9.73)$$

$$pK_a = 9.73.$$

Problem 12.14. A solution is prepared by dissolving 0.10 mole of NH_3 gas in enough water to make 1.0 litre of solution. What is the $[OH^-]$ in the resulting solution? K for the reaction $NH_4OH \rightleftharpoons NH_4^+ + OH^-$ is 1.8×10^{-5} mole/l.

Solution. For the equilibrium,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$K = \frac{[NH_4^+]\ [OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

Let $x = [NH_4^+]$ formed by the dissociation of NH_4OH.

$$x = [NH_4^+] = [OH^-]$$

$$[NH_4OH] = 0.10 - x$$

Assuming $x <<<< 0.10$

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5}$$

$$x = [OH^-] = 1.3 \times 10^{-3}M$$

Problem 12.15. Calculate the solubility of ethanoate in moles per dm^3 if the solubility product at 30°C is 4.9×10^{-3} $mol^2\ dm^{-6}$.

Solution. $CH_3COO^- Ag^+ \rightleftharpoons Ag^+ + CH_3COO^-$
ions in solution

$$K_s=[Ag^+][CH_3COO^-]=4.9\times10^{-3}=49\times10^{-4} \text{ mol}^2 \text{ dm}^{-6}$$

Since the ethonate and silver ions are produced in equal quantity in solution when the salt dissolves, the solubility of silver ethanoate is

$$s = [Ag^+]=[CH_3COO^-]=\sqrt{K_s}=\sqrt{(49\times10^{-4})}$$
$$s = 7\times10^{-2} \text{ mole}^{-3} \text{ dm}^{-3}$$
$$s = -(3.31)=-(-3+0.31)$$
$$s = +2.69.$$

Problem 12.16. To 35 cm³ of 0.02 mole dm^{-3} acetic acid were added 10 cm³ of 0.05 mole dm^{-3} sodium hydroxide. What is the pH of the solution? pK_a of acetic acid$=4.74$.

Solution. Let us express all quantities as their equivalent in cm³ of a 0.02 mole dm^{-3} solution.

Initial	*Final*
$Ac^- =$ negligible	$Ac^- \equiv$ NaOH added $=$ 10 cm³ of 0.05 mole dm^{-3} $=$ 25 cm³ of 0.02 mole dm^{-3}
$HAc = 35$	$HAc =$ Initial HAc$-$Ac$^-$produced $= 35-25=10.$

Thus in the final solution

$[Ac^-] =$ 25 cm³ of 0.02 mole dm^{-3} solution diluted to 45 cm³.
$[HAc] \equiv$ 10 cm³ of 0.02 mole dm^{-3} solution diluted to 45 cm³

$$\therefore \quad \frac{[Ac^-]}{[HAc]}=\frac{25}{10}=2.5$$

$$pH = 4.74+\log\frac{[Ac^-]}{[HAc]}$$
$$pH= 4.74+\log 2.5$$
$$pH= 5.14.$$

Problem 12.17. How many moles of sodium formate ($NaHCO_2$) must be added to 250 ml of a 1.0 M $HCHO_2$ solution to give a pH of exactly 4.00?

Solution. We know $[HCHO_2]=1.0$, and $[H^+]$ must be 1.0×10^{-4}, so we can solve for $[CHO_2^-]$ in the ionization constant expression

$$\frac{[H^+][HCO_2^-]}{[HCHO_2]}=\frac{[1.0\times10^{-4}][HCO_2^-]}{[1.0]}=2.1\times10^{-4}.$$
$$[CHO_2^-] = 2.1.$$

And if the number of moles per litre must be 2.1, the number of moles be added to 200 ml is $\frac{2.1}{4}=053$.

Problem 12.18. A 1.0M $Al(NO_3)_3$ solution is found to have a pH 2.70. Calculate K_a for the reaction:

$$Al^{3+} + HOH \rightleftharpoons Al(OH)^{2+} + H^+$$

Solution. pH 2.70, the $[H^+] = A \times 10^{-3}$, log *A* must be 0.30, so $[H^+] = 2.0 \times 10^{-3}$. From the hydrolysis equilibrium we see that if $[H^+] = 2.0 \times 10^{-3}$, $[AlOH^{2+}]$ must also be 2.0×10^{-3}, and $[Al^{3+}]$ would be $1.0 - 0.002 \simeq 1.0$ so

$$\frac{[AlOH^{2+}][H^+]}{[Al^{3+}]} = \frac{[2.0 \times 10^{-3}]\,[2.0 \times 10^{-3}]}{[1.0]}$$

$$= 4.0 \times 10^{-6}.$$

Problem 12.19. $AgNO_3$ is slowly added to a 0.020M solution of $NaC_2H_3O_2$,

(*a*) Will a precipitate of $AgC_2H_3O_2$ form, when conc. $[Ag^+] = 1 \times 10^{-2}$M?

(*b*) At approximately what $[Ag^+]$ will a precipitate start forming? The solubility product of $AgC_2H_3O_2$ is 2×10^{-3}.

Solution. (*a*) Let us calculate the product of the concentrations of Ag^+ and $C_2H_3O_2^-$ and compare it to $K_{sp}(2 \times 10^{-3})$

$$\text{conc. } Ag^+ \times \text{conc. } C_2H_3O_2^- = (1 \times 10^{-2})\,(2 \times 10^{-2})$$

$$= 2 \times 10^{-4}.$$

Since the concentration product is less than K_{sp} equilibrium is not established, and no silver acetate forms.

(*b*) As the precipitate begins to form, the concentration product, conc. $Ag^+ \times$ conc. $C_2H_3O_2^+$, must equal the equilibrium value, 2×10^{-3}. Neglecting dilution effects, the concentration of $C_2H_3O_2^-$ at that point must be 0.020M. Therefore $[Ag^+] \times 0.020 = 2 \times 10^{-3}$.

$$[Ag^+] = 0.10 \text{ M}$$

This is the minimum concentration of Ag^+ at which a precipitate will form. At higher Ag^+ ion concentrations precipitation will occur and sufficient $C_2H_3O_2^-$ ions will be removed from solution to maintain the concentration product at 2×10^{-3}.

Problem 12.20. Assuming that the addition of a small quantity of solid does not cause the volume of the solution to change, calculate the concentration of hydroxide ions in a solution made by dissolving 0.020 mole of ammonium chloride in 100 ml of 0.15M ammonia? K_{eq} for this reaction is 1.8×10^{-5}.

Solution. Ammonium chloride is a strong electrolyte and may be assumed to be completely ionized.

$$\therefore \quad [NH_4^+] = 1000 \text{ ml} \times \left(\frac{0.020 \text{ mole } NH_4^+}{100 \text{ ml}} \right)$$

$$= 0.20 \text{ mole}/l$$

$$\begin{array}{ll} NH_3+H_2O & \rightleftharpoons NH_4^+ + OH^- \\ 0.15M & \quad 0.02 \end{array}$$

For this reaction the equilibrium constant K_{eq} is given by

$$K_{eq} = \frac{[NH_4^+]\,[OH^-]}{[NH_2]}$$

$$1.8\times10^{-5} = \frac{[0.02]\,[OH^-]}{[0.15]}$$

$$[OH^-] = 1.4\times10^{-5}\text{M}.$$

Problem 12.21. Forty millilitres of 0.10 molar NaOH was added to ten millilitre of 0.45 molar HCl. What is the pH of the resulting solution? Both HCl and NaOH are strong electrolytes ($K_w = 1\times10^{-14}$ mole^2 litre^{-2}).

Solution.

	V (litre)	×*molarity (mole litre^{-1})*	= *number of moles*
NaOH	0.040	0.10	4.0×10^{-3}
HCl	0.010	0.45	4.0×10^{-3}

Both the substances are completely ionized in solution, therefore, 4.0×10^{-3} mole of each neutralizes the other. The total volume of the solution is 0.040+0.010=0.050 litre which contains 0.5×10^{-3} mole each of H^+ and Cl^- ions.

$$[H^+] = \frac{0.5\times10^{-8}\text{ mole}}{0.050\text{ litre}}$$

$$[H^+] = 1\times10^{-2}\text{ molar}$$

$$pH = -\log\,[H^+]$$

$$pH = -\log\,[10^{-2}]$$

$$pH = 2.$$

Problem 12.22. How many moles of sodium hydroxide can be added to one litre of a solution of 0.100 M in NH_3 and 0.100 M in NH_4Cl without changing pOH by more than one unit? Assume no change in volume. $K_b = 1.8\times10^{-5}$ and $pK_t = 4.75$.

Solution. $p\text{OH} = pK_b + \log\dfrac{[NH_4^+]}{[NH_3]}$

$$\therefore \quad \frac{[NH_4^+]}{[NH_3]} = 1.00$$

$$p\text{OH} = 4.75 + 0.000$$

$$p\text{OH} = 4.75.$$

The original pOH = 4.75. The pOH after addition of NaOH cannot be less than 3.75.

$$pOH = 3.75 = 4.75 + \log \frac{[NH_4^+]}{[NH_3]}$$

$$\log \frac{[NH_4^+]}{[NH_3]} = -1.00$$

$$\therefore \quad \frac{[NH_4^+]}{[NH_3]} = 0.10.$$

Hence NaOH can be added until the ratio of $[NH_4^+]$ to $[NH_3]$ is 0.10. Initially $[NH_4^+]+[NH_3] = 0.200$. Although the reaction with OH^- converts NH_4^+ into NH_3, the sum of the concentrations remains 0.200.

$$\begin{aligned} [NH_4^+]+[NH_3] &= 0.200 \\ [NH_4^+] &= 0.10\,[NH_3] \\ \therefore \quad 0.10\,[NH_3]+[NH_3] &= 0.200 \\ 1.10\,[NH_3] &= 0.200 \\ [NH_3] &= 0.182\text{ M} \\ \text{Hence} \quad [NH_4^+] &= 0.018\text{ M} \end{aligned}$$

Assuming no change in volume, $0.182-0.100=0.082$ moles of NaOH can be added without changing the pOH by more than 1.00 pOH unit.

Problem 12.23. Calculate the change in pH caused by dissolving 1.025 g of anhydrous sodium acetate in 100 cm^3 of 0.25 mole dm^{-3} acetic acid (molecular weight of anhydrous sodium acetate = 82; assume pK_a of acetic acid to be 4.74).

Solution. The initial concentration of acetic acid$=c=0.25$ mole dm^{-3}. Since acetic acid is a reasonably weak acid, the pH of its aqueous solution will be given by the equation

$$\begin{aligned} pH &= \tfrac{1}{2}\,pK_a - \tfrac{1}{2}\log C \\ pH &= \tfrac{1}{2}\,(4.74) - \tfrac{1}{2}\log 0.25 \\ \log 0.25 &= \bar{1}.4 = (-1+0.6) = -0.6 \\ pH &= \tfrac{1}{2}\,(4.74) - \tfrac{1}{2}\,(-0.6) \\ pH &= 2.37 + 0.3 = 2.67 \end{aligned}$$

Sodium acetate, being a salt of weak acid and strong base, is completely ionized, and 1.025 g dissolved in 100 cm^3 yields a solution containing $1.025/82 \times 100/1000$ mole dm^{-3} of acetate ions = 0.125 mole dm^{-3}. Thus in the final solution,

$$\begin{aligned} [Ac^-] &= 0.125 \text{ mole dm}^{-3} \\ [HAc] &= \text{initial } HAc = 0.25 \text{ mole dm}^{-3} \end{aligned}$$

Using the Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = 4.74 + \log \frac{[\text{Ac}^-]}{[HA\text{c}]}$$

$$\text{pH} = 4.74 + \log \frac{0.125}{0.25}$$

$$\text{pH} = 4.74 + \log 0.5$$

$$\log 0.5 = \bar{1}.7 = (-1+0.7) = -0.3$$

$$\text{pH} = 4.74 - 0.3 = 4.44$$

Increase in *p*H due to the addition of salt

$$= 4.4 - 2.6 = 1.77$$

Problem 12.24. One litre of a buffer (pH = 5.20) is to be prepared from NH_4Cl and NH_4OH. If 0.10 mole of NH_4Cl is used, how many moles of NH_3 should be added to the solution? Assume an activity coefficient of one.

Solution. $\text{pH} = 5.20$

$$p\text{OH} = 8.80 = -\log [\text{OH}^-]$$

$$[\text{OH}^-] = 1.6 \times 10^{-9}\text{M}$$

$$k = \frac{[\text{NH}_4{}^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$[\text{OH}^-] = 1.6 \times 10^{-9}\text{M}$; $[\text{NH}_4{}^+] = 0.10 + 1.6 \times 10^{-3}$

$[\text{NH}_4{}^+] = 0.10\text{M}$

Let $[\text{NH}_4\text{OH}] = x$

$$\therefore \frac{(1.6 \times 10^{-9})(0.10)}{x} = 1.8 \times 10^{-5} \text{ mole/l}$$

$$x = [\text{NH}_4\text{OH}] = 8.9 \times 10^{-6}\text{M}$$

$\therefore$ Add $8.9 \times 10^{-6} + 1.6 \times 10^{-9}$ mole of NH_3.

Problem 12.25. Calculate the pH of a solution prepared by mixing 0.10 mole of sodium acetate with enough water to make 1.0 litre of solution. Assume the activity coefficient of unity.

Solution. Since $K_h = \dfrac{K_w}{K_{\text{HAc}}} = \dfrac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]}$

Let x be the number of moles of acetic acid formed, then

$$[\text{HAc}] = x, \quad [\text{OH}^-] = x$$

$$[\text{Ac}^-] = 0.10 - x$$

Assuming $x <<< 0.10$

$$\therefore \frac{x^2}{0.10} = \frac{10^{-14}}{1.9 \times 10^{-5}}$$

$$x^2 = 5.3 \times 10^{-11} \text{ mole}^2/\text{l}^2$$

$$x = 7.3 \times 10^{-6}\text{M}$$

$$\text{pOH} = 5.14$$

$$\therefore \text{pH} = 14.0 - 5.14 = 8.86.$$

Problem 12.26. To 100 cm^3 of 0.1 mole dm^3 phosphate buffer pH 7.1 were added, (*a*) 1 cm^3 of 1.0 mole$^-$ dm^{-3} NaOH; (*b*) 5 cm^3 of 1.0 mole dm^{-3} NaOH; (*c*) 5 cm^3 of 0.1 mole dm^{-3} HCl.

Calculate the pH of the resulting solution in each case. The apparent pK_a values of phosphoric acid are 1.96, 6.8 and 12.

Solution. (*a*) Let us express all quantities in terms of cm^3 of a solution containing 0.1 mole dm^{-3}.

$\therefore$ NaOH added$\equiv$10 cm^3 of 0.1 mole dm^{-3} NaOH

which will convert an equivalent quantity of $H_2PO_4^-$ into HPO_4^{2-}.

Initial	*Final*
Volume = 100 cm^3	Volume = 101 cm^3
HPO_4^{2-} = 66.7	$HPO_4^{2-} \equiv (66.7+10)=76.7$
$H_2PO_4^-$ = 33.3	$H_2PO_4^- \equiv (33.3-10)=23.3.$

The pH of the final solution is given by the equation

$$pH = 6.8+\log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

where $[HPO_4^{2-}] \equiv$ 6.7 cm^3 of 0.1 mole dm^{-3} solution made up to 101 cm^3

$[H_2PO_4^-] \equiv$ 23.3 cm^3 of 0.1 mole dm^{-3} solution made up to 101 cm^3.

$$\log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}=\log\frac{76.7}{23.3}=0.52$$

$$pH=6.8+0.52=7.32.$$

(*b*) As we have seen above that addition to the buffer mixture of 3.33 cm^3 of 1 mole dm^{-3} NaOH is sufficient to convert it into the equivalent of 100 cm^3 of 0.1 mole dm^{-3} solution of $H_2PO_4^2$. Thus, when 5 cm^3 of 1 mole dm^{-3} NaOH is added, 1.67 cm^3 of 1 mole dm^{-3} NaOH remains to be neutralized by the HPO_4^{-2} acting as an acid when

$$HPO_4^{2-}+Na^+OH^- \rightleftharpoons \underset{\text{(conjugate base)}}{PO_4^{3-}}+Na^++H_2O$$

The pH of the resulting solution will therefore be determined by the 3rd dissociation constant of phosphoric acid according to the reaction,

$$HPO_4^{2-} \rightleftharpoons H^++PO_4^{3-}$$
$$pKa_3 = 12$$

and in a solution containing the conjugate pair HPO_4^{2-} and PO_4^{3-}

$$pH = 12.0+\log\frac{[PO_4^{3-}]}{[HPO_4^{2-}]}$$

Let us express all quantities in terms of cm^3 of a solution containing 0.1 mole dm^{-3}. Then, NaOH added ≡ 50, of which 33.3 are used to convert the whole of $H_2PO_4^-$ into HPO_4^2. However, the remaining 16.7 of NaOH will convert an equivalent quantity of HPO_4^{2-} into PO_4^{3-}.

Initially	*After addition of 33.3 NaOH*	*After further addition of 16.7 NaOH*
PO_4^{3-} = negligible	PO_4^{3-} = negligible	$PO_4^3 = 16.7$
$HPO_4^{2-} = 66.7$	$HPO_4^{2-} = 100$	$HPO_4^{2-} = 100-16.7$ $HPO_4^2 = 83.3$
$H_2PO_4^- = 33.3$	$H_2PO_4^-$ = negligible	$H_2PO_4^-$ = negligible

Therefore in the solution formed by the addition of 5 cm^3 of 1 mole dm^{-3} NaOH,

$[PO_4^{3-}] = 16.7$ cm^3 of a 0.1 mole dm^{-3} solution made up to 105 cm^3

$[HPO_4^{2-}] = 83.3$ cm^3 of a 0.1 mole dm^{-3} solution made up to 105 cm^3

$$\therefore \log \frac{[PO_4^{3-}]}{[HPO_4^{2-}]} = \log \frac{16.7}{83.3} = -3.7$$

$$pH = 12.0 + (-0.7) = 11.3.$$

(*c*) As we have seen in (*b*) that it would take 6.67 cm^3 of 1 mole dm^{-3} HCl to neutralize completely HPO_4^{2-} present in 100 cm^3 of 0.1 mole dm^{-3} phosphate buffer pH 7.1. Addition of only 5 cm^3 of 1 mole dm^{-3} HCl would produce a solution in which the conjugate pair is still $H_2PO_4^-$ and HPO_4^{2-} where

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$

$$pKa_2 = 6.8$$

$$\text{and, } pH = 6.8 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

Let us express all quantities in terms of cm^3 of a solution containing 0.1 mole dm^{-3}. Then HCl added ≡ 50, which is entirely consumed in converting an equivalent quantity of HPO_4^{2-} into $H_2PO_4^-$ according to the following reaction,

$$\underset{\text{(base)}}{HPO_4^{2-}} + HCl \rightarrow \underset{\text{(conjugate acid)}}{H_2PO_4^-} + Cl^-$$

Initial	*Final*
$HPO_4^{2-} = 66.7$	$HPO_4^{2-} = 66.7-50 = 16.7$
$H_2PO_4^- = 33.3$	$H_2PO_4^- = 33.3+50 = 83.3$

In the final solution formed by the addition of 5 cm^3 of 1 mole dm^{-3}

$$[HPO_4^{2-}] = 16.7 \text{ cm}^3 \text{ of a } 0.1 \text{ mole dm}^{-3}$$

solution made up to 105 cm^3.

$[H_2PO_4^-] \equiv 83.3$ cm^{-3} of a 0.1 mole dm^{-3} solution made up to 105 cm^3.

$$\log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \log \frac{16.7}{83.3} = -0.7$$

$$pH = 6.8 + (-0.7)$$

$$pH = 6.1.$$

EXERCISES

12.1. Among the following pHs which solution contains a weak acid?
(*i*) 1.72, (*ii*) 2.0, (*iii*) 3.7 (*iv*) 6.27. [**Ans.** 6.27.]

12.2. Among the following pHs which solution contains a strong acid?
(*i*) 1.72, (*ii*) 5.0, (*iii*) 6.38, (*iv*) 7.0, (*v*) 3.75 [**Ans.** 1.72]

12.3. The following compounds yield ions in solution as indicated. Are they acids, bases or salts?

(*i*) $Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$

(*ii*) $KOH \rightarrow K^+ + OH^-$

(*iii*) $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

(*iv*) $NH_4OH \rightarrow NH_4^+ + OH^-$

(*v*) $MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$

(*vi*) $Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$

[**Ans.** (*i*) salt, (*ii*) base, (*iii*) acid, (*iv*) base, (*v*) salt, (*vi*) base.]

12.4. Fill in the blanks:

(*i*) Bile has a pH range of 7.8 to 8.6, so it is a . . . . . . solution. (weak basic)

(*ii*) The pH of a saliva lies between 5.5 and 6.9 indicating a . . . . . . solution. (weak acid)

(*iii*) The gastric juices have a pH range of 1.6 to 1.8, so they are a . . . . . . solution. (strong acid)

(*iv*) Blood has a pH range of 7.35 to 7.45, so it is a . . . . . . solution. (weak basic)

(*v*) The pancreatic juices have a pH range of 7.5 to 8.0 so they are a . . . . . . solution. (weak basic)

12.5. Which of the following combinations would give buffer solution?
(*a*) $HNO_3 + NH_4NO_3$, (*b*) $NaNO_2 + NaOH$ (*c*) $HNO_2 + NaNO_2$
(*d*) $NH_4NO_3 + NH_4OH$ [**Ans.** (*c*) and (*d*)]

12.6. A buffer solution contains 0.20 mole of NH_4OH and 0.20 mole of NH_4Cl in 100 ml of solution. (*a*) What is the $[H^+]$ of the solution? (*b*) What is the pH after addition of 0.05 mole of HCl?

[**Ans.** (*a*) 1.8×10^{-5}; (*b*) 9.3.]

12.7. (*a*) Calculate the pH of a 0.2M KCN solution. The K_a for HCN is 4.9×10^{-10}. (*b*) What is the degree of hydrolysis of the salt?

[**Ans.** (*a*) pH=11.31, (*b*) 1.02 per cent.]

12.8. (*a*) What is the pH of 0.1M solution of monosodium succinate?
(*b*) What are the concentrations of unionized succinic acid, H succinate^{-1} and succinate^{-2} in the solution (pKa_1=4.19 and pKa=5.57)?
[Ans. (*a*) pH=4.88, (*b*) H_2 succinate=0.0146M, succinate^{-2} =0.0146M H succinate^{-1}=0.0709M.]

12.9. (*a*) Calculate the pH of 0.1M solution of NH_4Cl. The K_b for NH_4OH is 1.8×10^{-5}.
(*b*) What is the degree of hydrolysis of the salt?
[Ans. (*a*) pH=5.13, (*b*) 7.42×10^{-3} per cent.]

12.10. Calculate the pH of a 0.1M solution of KH_2PO_4. For H_3PO_4 $Ka_1=7.5\times10^{-3}$ and $Ka_2=6.2\times10^{-8}$.
[Ans. pH=4.6.7]

12.11. Compare the buffer capacity of a (*a*) 0.1M acetate pH 4.7, with that of a (*b*) 0.2M acetate buffer, pH 4.7. Assume that pK_a=4.7.
[Ans. (*a*)[H^+]=0.041M, (*b*) [H^+]=0.082M.]

12.12. Ten cm^3 of a solution of histidine at pH 7.5 was titrated with 0.1 mole dm^{-3} hydrochloric acid. After the addition of 36 cm^3 of acid, the pH was 6.0. Calculate the concentration of the histidine solution. (pK_a values of histidine are 1.8, 6.0, 9.3).
[Ans. 0.72 mole dm^{-3}.]

12.13. What is the maximum concentration of bicarbonate ions contained in (*a*) gastric, juice and (*b*) pancreatic juice, pH 7.8, if the concentration of carbonic acid in each 1 m mole dm^{-3}. [pK_a for carbonic acid is 6.1.]
[Ans. (*a*) 10^{-5} m mole dm^{-3}, (*b*) 5 m mole dm^{-3}.]

12.14. When a wide range of norcotics was tested on a longworm, the minimum anaesthetic dose of some of these compounds was found to vary with the prevailing pH. A selection of the results obtained is given below.
Minimum anaesthetic dose (mg/100 cm^3)

pH	*iso-amyl alcohol*	*cocaine*	*nembutal*
7	100	10	3
8	100	5	6
9	100	2.5	13

Can you explain these findings (qualitatively) in terms of effective ionic state of the narcotics? (Cocaine is a weak base, pK_b 5.6, nembutal is a weak acid pK_a 8.0).
[Ans. iso-amyl alcohol is non-ionizable and the pH does not determine what proportion of its molecules are present in the anaesthetically most effective form; cocaine is more effective anaesthetic in its basic form than its cationic form; nembutal is more effective in its acid form than in its anionic form.]

12.15. (*a*) Calculate the pH of a 0.05M solution of ethanolamine, $K_b=2.8\times10^{-5}$,
(*b*) What is the degree of ionization of the amine?
[Ans. (*a*) pH=11.07, (*b*) 2.36 per cent.]

12.16. Calculate the pH of a 0.2 M solution of an amine that has a pK_a of 9.5.
[Ans. pH=11.4.]

12.17. Calculate the ionic strength of 0.1M solution of butyric acid. $K_a=1.5\times10^{-5}$.
[Ans. 1.225×10^{-3}.]

12.18. Calculate the ionic strength of a 0.06 M potassium phosphate buffer. pH 7.5 (pK_a=7.2),
[Ans. 0.14.]

12.19. What is the maximum pH of a solution 0.10M in Mg^{2+} from which $Mg(OH)_2$ will not precipitate? K_{sp} for $Mg(OH)_2$ is 1.2×10^{-11}.
[Ans. pH=9.04.]

12.20. The solubility product of AgCl is 2.8×10^{-10} at 25°C. Calculate the solubility of the salts in (*i*) pure water, and (*ii*) 0.1M $AgNO_3$ solution.
[**Ans.** (*i*) 1.673×10^{-5} mole litre^{-1}, (*ii*) 2.8×10^{-9} mole litre^{-1}.]

12.21. Equal volumes of 1.0×10^{-2}M $CaCl_2$ and 4.0×10^{-4}M$-Na_2SO_4$ are mixed. Show with steps, whether a precipitate will be formed? Solubility product of calcium sulphate is 2.4×10^{-5}. Calculate the solubility of of calcium sulphate. [**Ans.** No. 0.4 mole litre^{-1}.]

12.22. Will CdS be precipitated from a solution containing 0.1 gram ion of Cd^{2+} and 0.3 g ion of H^+ions per litre when H_2S is passed into the solution? The K_{sp} of CdS is 3.6×10^{-29} and $(CH^+)^2\times CS^{2-}=1.1\times10^{-23}$. [**Ans.** Yes.]

12.23. Should precipitation occur when 50 mole of 5.0×10^{-4}M Ca $(NO_3)_2$ is mixed with 50 ml of 2.0×10^{-4}M NaF to give 100 ml of solution? The K_{sp} of CaF_2 is 1.7×10^{-10}. [**Ans.** No.]

12.24. If K_{hy} for F^- is 1.4×10^{-11} mole/l, what is $[H^+]$ in a solution prepared by dissolving 0.1 mole of NaF in enough water to make 500 ml of solution? [**Ans.** $[H^+]=5.9\times10^{-6}$.]

12.25. Sodium fluoride is a salt of the weak acid HF ($K_{diss}=6.9\times10^{-4}$ mole/l). What is K_{hy} for the F ion?
(**Hint** : Write the hydrolysis equations and then derive K_{hy} in terms of other constants). [**Ans.** 1.4×10^{-10}mole/l.]

12.26. The K_{sp} of $BaCrO_4$ is 3.0×10^{-10}. Find the molar concentration of CrO_4^{2-} ion in a saturated solution of $BaCrO_4$. [**Ans.** 1.73×10^{-5}.]

12.27. It is found that exactly 4.0×10^{-5} mole of strontium carbonate, $SrCO_3$ will dissolve per litre of solution. Find the K_{sp} of $SrCO_3$. [**Ans.** 1.60×10^{-9}]

12.28. A chemist has a solution containing Br^-, Cl^-, and I^-. He wishes to precipitate most of the iodide ion but leave the bromide and chloride ions in solution. K_{sp}'s of AgCl, AgBr, and AgI are 1.0×10^{-10}, 5.0×10^{-13} and 1.0×10^{-16} respectively. If the solution is 0.10M in Cl^-, Br^-, and I^-, show how he could do this?
[**Ans.** Add Ag^+until $[Ag^+]=1.0\times10^{-12}$, At that point $[I^-]=10\times10^{-4}$ while concentration of Br^- and Cl^-remain 0.10M.]

12.29. A saturated solution of Ag_3AsO_4 was found to contain 1.0×10^{-8} mole of AsO_4^{-3} ions and 3.0×10^{-6} mole of Ag^+ions per litre of solution. What is K_{sp} for Ag_3AsO_4? [**Ans.** 2.7×10^{-23}.]

12.30. A solution is saturated with respect to $BaSO_4$ ($K_{sp}=1.1\times10^{-10}$) and BaF_2 ($K_{sp}=1.7\times10^{-6}$). Find $[SO_4^{2-}]$ in the solution if $[F^-]=4.1\times10^{-2}$M.
[**Ans.** 1.2×10^{-7} M.]

12.31. A solution is originally 0.01M in acetate ion, $C_2H_3O_2^{2-}$, and 0.01M in sulphate ion, SO_4^{2-}. Solid silver nitrate is added until $[Ag^+]=4.0\times10^{-2}$ in the solution. Find $[C_2H_3O_2^-]$ and $[SO_4^{2-}]$ after the $AgNO_3$ is added.
[**Ans.** $(C_2H_3O_2^-)=0.01$M; $(SO_4^{2-})=0.01$M.]

12.32. Exactly 500 ml of 0.1N ammonium hydroxide is combined with 100 ml of 0.5N HCl. Calculate the final pH of the solution. [**Ans.** 5.2.]

12.33. What is the pH of a 0.05M solution of sodium borate at 25°C? What would be the pH of the same solution at 5°C? The pK_a of boric acid is 9.44 at 5°C and $pK_w=14.73$ at 5°C. [**Ans.** 25°C, 10.96; 5°C, 11.44.]

12.34. 500 ml of 0.2M propionic acid is mixed with 500 ml of 0.2M KOH. What is the pH of the solution? [**Ans.** 8.93.]

12.35. Calculate the PO_4^{3-} concentration in a 0.1M H_3PO_4 solution at 25°C.
[**Ans.** 1.05×10^{-18}M.]

12.36. The ionization constant of water, K_w at 37°C is 2.42×10^{-14} mole^2 litre^{-2}. What is the pH for a neutral solution at this normal temperature of the human body? [Ans. 6.8.]

12.37. Calculate the ionic product of water at 25°C given that the pH of a 0.05 mole dm^{-3} aqueous solution of sodium acetate is 8.64 at this temperature and that the ionization constant of acetic acid is 1.75×10^{-5}. Use the extended form of the Debye Huckel equation, $\log_{10} y = -\dfrac{Az^2\sqrt{I}}{1+\sqrt{I}}$, to estimate activity coefficients. [Ans. $K_w=0.98\times10^{-14}$.]

12.38. If a very small amount of phenolphthalein is added to a 0.15 mole dm^{-3} solution of sodium benzoate, what fraction of the indicator will exist in the coloured form? State any assumptions that you make.

K_a (Benzoic acid)$=6.2\times10^{-5}$

$K_w(H_2O)=1.0\times10^{-14}$

K_{I_n} (phenolphthalein$=3.16\times10^{-10}$

[Ans. 0.16: the activity coefficients are neglected and it is assumed that the coloured tautomeric form of the indicator is completely ionized]

12.39. Estimate the volume of 0.1 mole dm^{-3} sodium hydroxide which must be added to 200 cm^3 of 0.1 mole dm^{-3} acetic acid ($K_a=1.75\times10^{-5}$) to give a solution with a pH of 6.0. Give a suitable choice of the indicator for the titration of acetic acid with sodium hydroxide.

[Ans. 190 cm^3; phenolphthalein ($pK_{I_n}=9.5$).]

12.40. Calculate the pH of an aqueous solution of ethyl ammonium acetate at 25°C, given the following equilibrium constants

K_a (acetic acid) $=1.75\times10^{-2}$

K_b (ethylamine) $=4.7\times10^{-4}$

$K_w=1.01\times10^{-14}$

[Ans. 7.7..]

12.41. At 25°C, the dissociation constant of benzoic acid in water is 6.3×10^{-5} and the ionic product of water is 1.01×10^{-14}. Calculate the pH of (*a*) 0.01 mole dm^{-3}, and (*b*) 0.1 mole dm^{-3} aqueous solution of sodium benzoate (*i*) taking all activity coefficients to be unity, and (*ii*) taking the activity coefficients of the monovalent ions to be 0.9 and 0.01 mole dm^{-3} solution and 0.8 in 0.1 ml dm^{-3} solution.

[Ans. (*a*) (*i*) pH 8.10, (*ii*) pH 8.05, (b) (*i*) pH 8.60, (*ii*) pH 8.50.]

12.42. The experimental values of pK for very dilute ATP at 25°C and 0.2 ionic strength are 6.95 in tetra-*n*-propyl ammonium chloride and 6.41 in NaCl. What is the standard Gibbs free energy for the reaction

$$NaATP^{3-} \rightleftharpoons Na^+ + ATP^{4-}$$

assuming $HATP^{3-}$ does not bind Na^+ significantly?

[Ans. 1.5 k. cal. mole^{-1}.]

12.43. The hydrolysis of adenosine triphosphate ATP to adenosine diphosphate ADP and inorganic phosphate at pH 8 and 25°C,

$$ATP^{4-}+H_2O=ADP^{3-}+HPO_4^{2-}+H^+$$

has a standard enthalpy change of -3 k. cal. The standard enthalpy changes of acid dissociation of $HATP^{-3}$, $HADP^{-2}$, $H_2PO_4^{-1}$ are -2, 0, and $+2$ k. cal. mole^{-1}, respectively. Calculate the standard enthalpy change for the reaction:

$HATP^{-3}+H_2O=HADP^{-2}+H_2PO_4^-$ [Ans. -7 k cal mole^{-1}]

13

ELECTROCHEMICAL CELLS

INTRODUCTION

A chemical reaction is normally accompanied by a transfer of energy between the reacting system and the environment. Although this transfer is usually achieved by the evolution or absorption of heat energy, it is possible to arrange for some of the energy transferred from the system to environment to do work. A voltaic cell is the most common device used for the purpose. However, the proportion of total energy available for the reaction, which takes place in the cell, can be varied by suitably adjusting the circuit in which the cell is connected, but there is an upper limit to this energy.

Cell diagrams. It is convenient to have a simple method of representing a given voltaic cell. This is called a cell diagram. It indicates the constituents of the cell, where the porous partition is placed, the materials which constitute the terminals, and their polarity. The convention agreed by the International Union of Pure and Applied Chemistry (IUPAC) is used for cell diagrams. The interfaces between solutions and solid terminal materials are represented by the solid vertical lines, the porous partition or salt bridge by a vertical broken line and the sign preceding the emf value indicates the polarity of the right hand terminal. Galvanic cells are made by arranging for a spontaneously occurring oxidation-reduction reaction to proceed in such a way that electrons are transferred from the reducing agent to the oxidising agent by means of an outside or external circuit. A typical galvanic cell might consist of a zinc rod dipping into a solution of its ions and copper rod dipping into a solution of copper ions. On the IUPAC convention the Daniell cell can be represented as in one of the following two ways,

$$\mathrm{Zn(c)} \mid \mathrm{Zn^{2+}(aq.)} : \mathrm{Cu^{2+}(aq.)} \mid \mathrm{Cu(c)}\ ; \qquad E = +1.1\mathrm{V}$$

$$\mathrm{Cu(c)} \mid \mathrm{Cu^{2+}(aq.)} : \mathrm{Zn^{2+}(aq.)} \mid \mathrm{Zn(c)}\ ; \qquad E = -1.1\mathrm{V}$$

In the Daniell cell, the terminals (zinc and copper) take part in the cell reaction.

In general there are two types of galvanic cells:

1. Chemical cells
2. Concentration cells.

Chemical energy can be converted into electrical energy when a redox reaction is carried out with reactants separated in space and connected only by an electrical conductor.

A difference in potential causes current to flow from an electrode of higher potential to one of lower potential. This difference is called the electromotive force (emf). Since the absolute value for the emf of a single half-cell reaction cannot be determined it is related to the reference electrode. The reference is the hydrogen electrode which has a defined emf of 0.00. The emf of any other electrode reaction can be determined by measuring the emf of a cell constructed from the electrode in question, and the hydrogen electrode. The standard reduction potentials of some systems are given in Table 13.1.

TABLE 13.1: Standard reduction potentials

Reduction half-reaction	*Standard reduction potential (volts)*
$Li^+ + e^- \rightarrow Li$	−3.05
$Na^+ + e^- \rightarrow Na$	−2.71
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.25
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.15
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.07
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
$Au^{3+} + 3e^- \rightarrow Au$	+1.50
$F_2 + 2e^- \rightarrow 2F^-$	+2.87

Method of predicting the spontaneity of a reaction

The free energy change ΔG in a cell is related to the spontaneity of the reaction. Spontaneous reactions will have a negative value for the free energy change ΔG.

Whether a given oxidation-reduction reaction is spontaneous or not is indicated by the value of the free energy function ΔG°.

$$\Delta G^\circ = -nE^\circ F \qquad \ldots (1)$$

where n is the number of electrons transferred, E° is the standard potential for the reaction and F is the faraday. For a direct conversion between ΔG° in k. cal. and E° in volts, the equation is

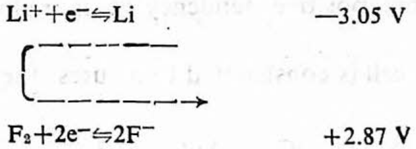
$$\Delta G^\circ = -23.06nE^\circ \qquad \ldots (2)$$

Standard potentials can also be related to equilibrium constants by the following relation,

$$\Delta G^\circ = -23.06nE^\circ = -RT\ln K \qquad \ldots (3)$$

$$nE^\circ = 0.0592 \log K \qquad \ldots (4)$$

Given a list of reduction potentials (*see* Table 13.1) spontaneous reactions will occur only according to anti-clockwise arrow shown in Figure 13.1



$Li^+ + e^- \rightleftharpoons Li$
−3.05 V
$F_2 + 2e^- \rightleftharpoons 2F^-$
+2.87 V

Fig. 13.1.

Li will be oxidised by F_2 to give Li^+ and F_2 will be reduced to F^-. Any reducing agent higher on the right hand side of the table will react with any oxidising agent lower on the left hand side of the table. Under standard conditions, all oxidation-reduction reactions obey the AC (anticlockwise) rule. It is a qualitative device to help us, remember the fundamental point that a reaction will be spontaneous if the sum of the appropriate potentials is positive.

Nernst equation. This equation gives us a relationship between the oxidation potential E of any reversible electrode and E° the corresponding standard oxidation potential i.e.,

$$E = E^\circ_{el} - \frac{RT}{nF} \ln \frac{(\text{Oxidised state})}{(\text{Reduced state})} \qquad \ldots (5)$$

or

$$E = E^\circ_{el} - \frac{0.059}{n} \log \frac{(\text{Oxidised state})}{(\text{Reduced state})} \qquad \ldots (6)$$

One of the most interesting applications of electrode potentials is in connection with potentiometric titration. In this method the end point of a titration is determined by measurement of electrode potential. The change of potential is small in the beginning. However, when the end point of titration is approached there is a much rapid change of potential. The end point can thus be found by determining the quantity of titrant added when the rate of change in electrode potential is maximum. The potentiometric procedure can be employed with coloured solutions and often in dilute solutions at which ordinary titrations with coloured indicator would be quite inaccurate.

Problem 13.1. A cell is constructed using Zn and Zn^{2+} in one half-cell and Ni with Ni^{2+} in the other half-cell. Write the reaction and find the standard patential of the cell.

Solution. Both reduction potentials are negative, but the zinc potential is more negative. The half-reactions, the total reactions and the standard potentials are

$$
\begin{array}{ll}
Ni^{2+}+2e^- \rightarrow Ni & -0.25\ V \\
Zn \rightarrow Zn^{2+}+2e^- & +0.76\ V \\
\hline
Ni^{2+}+Zn \rightarrow Ni+Zn^{2+} & +0.51\ V
\end{array}
$$

Since nickel has more positive tendency it is reduced and zinc is oxidised.

Problem 13.2. A cell is constructed that uses the following half-reactions

$$Au(s)+4Cl^- \rightarrow AuCl_4^-+3e^-$$
$$Au^{3+}+3e^- \rightarrow Au(s)$$

The standard potential of the cell is found to be +0.50 volt. Calculate the equilibrium constant for the reaction

$$Au^{3+}+4Cl^- \rightleftharpoons AuCl_4^-$$

Solution. The standard potential for the oxidation in this case is —1.00 V, for the reduction it is +1.50 V, and $E°$ for the cell is +0.50V

$$
\begin{array}{ll}
Au(s)+4Cl^- \rightarrow AuCl_4^-+3e^- & -1.00\ V \\
Au^{3+}+3e^- \rightarrow Au(s) & +1.50\ V \\
\hline
Au^{3+}+4Cl^- \rightarrow AuCl_4^- & +0.50\ V
\end{array}
$$

The number of elections transferred in the cell is 3.

$$\Delta G° = -23.06 nE°$$
$$nE° = 0.0592 \log K$$
$$\log K = \frac{(3)\,(+0.50)}{0.0592} = 25.34.$$
$$\log K = 25+0.34$$
$$K = 2.2 \times 10^{25}$$

Hence the equilibrium lies far to the right and $AuCl^-_4$ is thus a very stable complex ion.

Problem 13.3. A voltaic cell is constructed using Al and Al^{3+} in one half-cell, and Ag and Ag^+ in the other half-cell. (*a*) What total reaction will occur? (*b*) What half-reaction will occur at each electrode? (*c*) Which is the anode and which is the cathode? (*d*) How many volts will the cell produce if [Al^{3+}] and [Ag^+] are 1.0 M?

Solution. (*a*) The reduction potential for Ag is positive, relative to hydrogen, and the reduction potential for aluminium is negative. Therefore, silver will be reduced and Al will be oxidized. The balanced equation for the reaction is

$$Al+3Ag^+ \rightleftharpoons Al^{3+}+3Ag$$

(*b*) The half-reactions are

$$Al \rightarrow Al^{3+}+3e^-$$
$$3Ag^++3e^- \rightarrow Ag$$

(*c*) Since the oxidation occurs at the Al electrode, this is called the anode. Reduction occurs at the Ag electrode and is called the cathode.

(*d*) The voltage, or potential difference, produced by the cell is just the total difference between the standard potentials for Al and Ag. The standard reduction potential for Al is—1.66 V and for Ag it is +0.80 V. The total difference is 2.46. This is the voltage produced by the cell.

Problem 13.4. In the lead storage battery, the anode reaction is

$$Pb(s)+HSO_4^-+H_2O \rightarrow PbSO_4(s)+H_3O^++2e^-$$

A typical battery would be rated "100 ampere-hours" which means it has the chemical capacity to deliver 100 ampere for 1 hour or 1 ampere for 100 hours. How many grams of lead would be used up at the foregoing anode to accomplish this?

Solution. 1 ampere for 100 hours is,

$$= \left(\frac{1C}{sec}\right)(100 \text{ hours}) \left(\frac{60 \text{ min}}{\text{hour}}\right)\left(\frac{60 \text{ sec}}{\text{min}}\right)$$
$$= 3.6\times10^5 C$$

This many number of coulombs is equal to

$$\frac{3.6\times10^5 C}{96{,}500 C/\text{faraday}}$$
$$= 3.73 \text{ faradays.}$$

The half-reaction says that 1 mole of lead disappears for each 2 faradays liberated. If 3.73 faradays are liberated this is equal to

$$= (3.73 \text{ faradays}) \ \frac{1 \text{ mole of lead}}{2 \text{ faradays}}$$
$$= 1.86 \text{ moles of lead}$$
$$= 1.86 \text{ moles of lead } (207.19 \text{ g/mole})$$
$$= 385 \text{ g.}$$

Problem 13.5. Calculate E for the reaction $2H_2(g)+O_2(g)\rightarrow 2H_2O$, when $pH_2=5.0$ atm, $pO_2=2.5$ atm $H_3O^+=0.60$ m.

Solution. The above reaction may be written as,

$$\begin{array}{ll} H_2(g)+2H_2O\rightarrow 2H_3O^+ + 2e^- & E^\circ=0.00 \\ \underline{O_2(g)+4H_3O^+ + 4e^-\rightarrow 6H_2O} & E^\circ=+1.23\text{ V} \\ 2H_2(g)+O_2(g)\rightarrow 2H_2O & E^\circ=+1.23\text{ V} \end{array}$$

$$E=E^\circ-\frac{0.0592}{n}\log\frac{1}{p^2H_2.pO_2}\text{ when } n=4$$

$$E=+1.23-\frac{0.0592}{4}\log\frac{1}{(5.0)^2(2.5)}$$

$$E=+1.26\text{ V}.$$

Problem 13.6. What happens to voltage of the hydrogen electrode when the molality of H_3O^+ is cut to 10^{-2} m assuming the hydrogen pressure stays at 1 atm?

Solution. $H_2(g)+2H_2O\rightarrow 2H_3O^+ + 2e^-$; $E^\circ=0.0$

$$E=E^\circ-\frac{0.0592}{2}\log\frac{m^2H_3O^+}{pH_2}$$

where $m_{H_3O^+}=10^{-2}$ and $pH_2=1.0$

$$\therefore\ E=0-0.0296\log\frac{(10^{-2})^2}{1{\cdot}00}$$

$$E=-0.0296\log 10^{-4}=+0.118\text{ V}.$$

Problem 13.7. Calculate K_{eq}. for the reaction

$$2Cr+3Fe^{2+}\rightarrow 2Cr^{3+}+3Fe$$

$$K_{eq}=\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$E^\circ_{Cr-Cr^{3+}}=0.71\text{ volts}$$

$$E^\circ_{Fe^{2+}-Fe}=-0.44\text{ volts}.$$

Solution. Half-reactions

$$\begin{array}{ll} 2Cr\rightarrow 2Cr^{3+}+6e^+ & E^\circ=0.71\text{ volts} \\ 3Fe^{2+}+6e^+\rightarrow 3Fe & E^\circ=-0.44\text{ volts} \end{array}$$

$$n=6$$

$$E^\circ_{ox}+E^\circ_{red}=0.71-0.44$$

$$=+0.27\text{ volts}$$

$$K_{eq}.=\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$E^\circ_{ox}+E^\circ_{red}=\frac{0.059}{n}\log K_{eq}.$$

$$\log K_{eq}.=\frac{0.27}{0.059/6}$$

$$K_{eq}=10^{27}.$$

Problem 13.8. Calculate the potential for each half-cell and the total emf at 25°C for the cell represented schematically as

$$Pb \mid Pb^{2+}(0.0010\text{ M}) \mid Pt, Cl_2\ (1\text{ atm}) \mid Cl^-(0.10\text{ M})$$

$$E^\circ_{Pb-Pb^{2+}} = +0.126 \text{ volts}$$

$$E^\circ_{Cl_2-2Cl^-} = +1.358 \text{ volts.}$$

Solution. At anode:

$$E_{ox} = E^\circ_{Pb-Pb^{2+}} - \frac{0.059}{n} \log \frac{[Pb^{2+}]}{[Pb]}$$

$$E_{ox} = +0.126 - \frac{0.059}{2} \log [0.0010]$$

$$E_{ox} = 0.126 - 0.030\ (-3.0)$$

$$E_{ox} = +0.216 \text{ volts}$$

At cathode:

$$E_{red} = E^\circ_{Cl_2-2Cl^-} - \frac{0.059}{n} \log \frac{[Cl^-]^2}{P\ c}$$

$$E_{red} = +1.36 - \frac{0.059}{2} \log [0.10]^2$$

$$E_{red} = 1.36 - 0.030\ (-2)$$

$$E_{red} = +1.42 \text{ volts.}$$

Cell:

$$E = E_{ox} + E_{red}$$

$$E = 0.216 + 1.42 = +1.64 \text{ volts.}$$

Problem 13.9. The emf of the cell

$$Zn \mid ZnCl_2\ (0.05 \text{ mole dm}^{-3}) \mid AgCl(s), Ag$$

is 1.015 V at 298 K, the silver electrode being positive, whilst the temperature coefficient of its emf is -0.000492 VK^{-1}. Write down the equation for the reaction occurring when the cell is allowed to discharge and calculate the changes in (*a*) free energy $\triangle G$, and (*b*) heat content $\triangle H$, and (*c*) entropy accompanying this reaction, at 298 K.

Solution. At the cathode (—) $Zn \rightarrow Zn^{2+} + 2e^-$

At the anode (+)

$$\frac{2AgCl(s) + 2e \rightarrow 2Ag + 2Cl^-}{Zn + 2AgCl(s) \rightarrow 2Ag + Zn^{2+} + 2Cl^-}$$

(*a*) The free energy change accompanying the reaction is given by

$$\triangle G = -nEF$$

$$n = 2, \quad E = 1{,}015 \text{ V}, \ F = 96500 \text{ C mole}^{-1}$$

$$\triangle G_{298k} = -2 \times 1.015 \text{ V} \times 96500 \text{ C mole}^{-1}$$

$$\triangle G_{298k} = -196000 \text{ J mole}^{-1}$$

$$\triangle G_{298k} = -196 \text{ kJ mole}^{-1}$$

(*b*) The Gibbs-Helmholtz equation takes the form,

$$\triangle G=\triangle H+T\left[\frac{\partial(\triangle G)}{\partial V}\right]_P$$

Since $\triangle G=-nEF$

$$\triangle H=-nEF+nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\triangle H_{298\text{k}}=-196 \text{ kJ mole}^{-1}+\frac{2\times 96500\times 290\times 0.000492}{1000} \text{ kJ mole}^{-3}$$

$$\triangle H_{298\text{k}}=-224 \text{ kJ mole}^{-1}$$

(*c*) $\triangle G=\triangle H-T\triangle S$

$$\triangle S=\frac{\triangle H-\triangle G}{T}$$

$$\triangle S_{298\text{k}}=nF\left(\frac{\partial E}{\partial T}\right)_P$$

$$\triangle S_{298\text{k}}=-2\times 96500\times 0.000492 \text{ JK}^{-1}\text{ mole}^{-1}$$

$$\triangle S_{298\text{k}}=-95.0 \text{ JK}^{-1}\text{ mole}^{-1}.$$

Problem 13.10. The equivalence point in the titration of 40.00 ml solution of a weak monoprotic acid occurs when 35.00 ml of a 0.100 N NaOH solution has been added. The pH of the solution is 5.75 after 20.00 ml of the NaOH solution has been added. What is the dissociation constant of the acid?

Solution. Since for the complete neutralization of the acid 35.00 ml of NaOH is required. Therefore on adding 20 ml of NaOH, $\frac{20}{35}$ of the acid has been neutralized. In other words, this means that $\frac{15}{35}$ of the acid is in the form HA, and $\frac{20}{35}$ is in the form A^-

$\therefore$ The ratio $\frac{[HA]}{[A^-]}=\frac{15}{20}$

$$=0.75.$$

$$\text{pH}=pK-\log\frac{[HA]}{[A^-]}$$

$$5.75=pK-\log(0.75)$$

$$pK=5.63$$

$$K=2.4\times 10^{-6}.$$

Problem 13.11. A 50.0 ml sample of 0.10 M ferrous sulphate is titrated with 0.10 M ceric sulphate. (*a*) What is the equilibrium constant for the reaction? (*b*) What are the concentrations of ions in equilibrium at the equivalence point?

Solution. (*a*) The electrode potentials for the half-reactions are

$Fe^{3+}+e^-\rightleftharpoons Fe^{2+}$ $E^\circ=+0.77$ V

$Ce^{4+}+e^-\rightleftharpoons Ce^{3+}$ $E^\circ=+1.61$ V

The potential for the reaction is

$$Fe^{2+}+Ce^{4+} \rightleftharpoons Fe^{3+}+Ce^{3+} \quad E^\circ=+0.84 \text{ V}$$

Since $\triangle G^\circ = -RT \ln K$

and $E^\circ = \dfrac{0.05916}{n} \log K$

$$\log K = 16.9\, nE^\circ$$
$$K = 16.9(1)\,(0.84)$$
$$K = 1.6 \times 10^{14}.$$

(*b*) At the equivalence point we have

$$[Fe^{3+}] = [Ce^{3+}]$$

and $[Fe^{2+}] = [Ce^{4+}]$

$$K = \frac{[Fe^{3+}][Ce^{3+}]}{[Fe^{2+}][Ce^{4+}]}$$
$$K = 1.6 \times 10^{14}$$
$$\frac{[Fe^{3+}]^2}{[Fe^{2+}]^2} = 1.6 \times 10^{14}$$
$$\therefore \quad \frac{[Fe^{3+}]}{[Fe^{2+}]} = 1.3 \times 10^7$$

Since the volume of the solution equals 100 ml at the equivalence point, $[Fe^{3+}]=[Cl^{3+}]=0.050$ M.

Let $x=[Fe^{2+}]=[Ce^{4+}]$

$$\therefore \quad \frac{0.050}{x} = 1.3 \times 10^7$$
$$\therefore \quad x = [Fe^{2+}] = [Ce^{4+}] = 3.8 \times 10^{-9} \text{ M}$$

and $[Fe^{3+}] = [Ce^{3+}] = 5.0 \times 10^{-2}$ M.

Problem 13.12. The temperature dependence of the emf of an electro-chemical cell can often be written in the form

$$E = (a + bT + cT^2 + dT^3) \text{ volt}$$

where a, b, c and d are constants. A certain commercially suitable battery was found to have $a=1.19237$, $b=-1.537 \times 10^{-4}$, $c=2.73 \times 10^{-8}$ and $d=1.78 \times 10^{-11}$. Calculate $\triangle G$, $\triangle H$ and $\triangle S$ for this cell at 27°C if $n=3$.

Solution. $\triangle G = -nEF$

where $n=3$

$F=96{,}487$ coulombs is equal to 23.06 k. cal. volt^{-1} equiv^{-1}

$$\triangle G = -3(23.06)\,[1.19237 - (1.537 \times 10^{-4})\,(300) + (2.73 \times 10^{-8})\,(300)^2 + (1.78 \times 10^{-4})\,(300)^3]$$
$$= -79.52 \text{ k. cal.}$$
$$\triangle S = nF \frac{\partial E}{\partial T}$$
$$= nF(0 + b + 2cT + 3dT^2)$$

$$\Delta S = 3(23.06)[-1.537\times10^{-4}+2(2.73\times10^{-8})T]$$
$$+3(1.78\times10^{-11})T^2$$
$$\Delta S = -9.17 \text{ cal. deg}^{-1}.$$
$$\Delta H = \Delta G + T\Delta S$$
$$\Delta H = -79.52+300\ (-9.17\times10^{-3})$$
$$\Delta H = -82.27 \text{ k. cal.}$$

EXERCISES

13.1. Which of the following reactions will occur spontaneously? Use Table 13.1 of reduction potentials.

(*a*) $H_2+Sn^{2+} \rightleftharpoons 2H^++Sn^{4+}$
(*b*) $Fe+Co^{2+} \rightleftharpoons Fe^{2+}+Co$
(*c*) $Au+3Ag^+ \rightleftharpoons Au^{3+}+3Ag$
(*d*) $2Cu^+ \rightleftharpoons Cu+Cu^{2+}$
(*e*) $2Br^-+\frac{1}{2}O_2+2H^+ \rightleftharpoons Br_2+H_2O$
(*f*) $Br_2+Cu^{2+} \rightleftharpoons 2Br^-+Cu$
(**Hint.** Apply AC rule).

[**Ans.** (*b*), (*d*) and (*e*) are spontaneous.]

13.2. Complete and balance the following oxidation-reduction reactions (in acid solution).

(*a*) $SO_2+Cr_2O_7^{-2} \rightleftharpoons SO_4^{2-}+Cr^{3+}$
(*b*) $I^-+NO_3^- \rightleftharpoons I_2+NO$
(*c*) $ClO_3^- \rightleftharpoons ClO_4^-+Cl^-$
(*d*) $F_2+H_2O \rightleftharpoons F^-+O_2$
(*e*) $S_2O_3^{-2}+MnO_4^- \rightleftharpoons S_4O_6^{2-}+Mn^{2+}$

[**Ans.** (*a*) $3SO_2+2H^++Cr_2O_7^{2-} \rightleftharpoons 3SO_4^{2-}+2Cr^{3+}+H_2O$
(*b*) $I^-+8H^++2NO_3^- \rightleftharpoons 3I_2+2NO+4H_2O$
(*c*) $4ClO_3^- \rightleftharpoons 3ClO_4^-+Cl^-$
(*d*) $2F_2+2H_2O \rightleftharpoons O_4+4H^++4F^-$
(*e*) $10S_2O_3^{2-}+16H^++2MnO_4^- \rightleftharpoons 5S_4O_6^{2-}+2Mn^{2+}+8H_2O$.]

13.3. Calculate ΔG° and the equilibrium constant for the reaction

$$Fe+Ni^{2+} \rightleftharpoons Fe^{2+}+Ni$$

For,
$$Fe \rightarrow Fe^{2+}+2e^- \quad E^\circ = +0.44V$$
$$Ni^{2+}+2e^- \rightarrow Ni \quad E^\circ = -0.25V$$

[**Ans.** −8.76 k. cal. 2.6×10^6.]

13.4. Represent schematically a cell which has the overall chemical reaction

$$Cu+2H^+ \rightarrow Cu^{2+}+H_2(g)$$

The concentration of H^+ ions and Cu^{2+} ions in solution is 1 M and the pressure of H_2 is 1 atm.

[**Ans.** $Cu \mid Cu^{2+}$ (1 M) $\|$ H^+ (1 M) $\mid$ H_2(1 atm), Pt.]

13.5. In a cell the electrons flow from Pt to Cu, write the anode and cathode reactions. [**Ans.** Cathode $Cu^{2+}+2e^- \rightarrow Cu$ Anode $H_2 \rightarrow 2H^++2e^-$.]

13.6. Write the equations for the reactions at the left-hand electrode; the reaction at the right hand electrode; and the overall cell reaction, for each of the following galvanic cells

(*a*) $Mg \mid Mg^{2+} \parallel Cu^{2+} \mid Cu$
(*b*) $Mg \mid Mg^{2+} \parallel Zn^{2+} \mid Zn$
(*c*) $Cd \mid Cd^{2+} \parallel Hg^{2+} \mid Hg$
(*d*) $Pt \mid H_2 \mid H_3O^+ \parallel Zn^{2+} \mid Zn$
(*e*) $Pt \mid H_2 \mid H_3O^+ \parallel Cu^{2+} \mid Cu$
(*f*) $Pt \mid Br_2 \mid Br^- \parallel Fe^{2+}, Fe^{3+} \mid Pt$

[**Ans.** (*a*) $Mg \rightarrow Mg^{2+} + 2e^-$
$Cu^{2+} + 2e^- \rightarrow Cu$
$Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$
(*b*) $Mg \rightarrow Mg^{2+} + 2e^-$
$Zn^{2+} + 2e^- \rightarrow Zn$
$Mg + Zn^{2+} \rightarrow Mg^{2+} + Zn$
(*c*) $Cd \rightarrow Cd^{2+} + 2e^-$
$Hg_2 + 2e^- \rightarrow 2Hg$
$Cd + Hg_2^{2+} \rightarrow Cd^{2+} + 2Hg$
(*d*) $2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$
$Zn \rightarrow Zn^{2+} + 2e^-$
$2H_3O^+ + Zn \rightarrow H_2 + 2H_2O + Zn^{2+}$
(*e*) $H_2 + 2H_2O \rightarrow 2H_3O^+ + 2e^-$
$Cu^{2+} + 2e^- \rightarrow Cu$
$H_2 + 2H_2O + Cu^{2+} \rightarrow 2H_3O^+ + Cu$
(*f*) $Br_2 + 2e^- \rightarrow 2Br^-$
$Fe^{2+} \rightarrow Fe^{3+} + e^-$
$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$].

13.7. Calculate the electrode potential of Zn^{2+}/Zn electrode in which the concentration of Zn^{2+} ions is 0.1M? [**Ans.** -0.76V].

13.8. (*a*) Calculate the potential for the cell
$Ni \mid Ni^{2+}(0.01M) \parallel Cl^-(0.2M) \mid Cl_2$ (1 atm) Pt
(*b*) What is ΔG for the cell reaction? [**Ans.** (*a*) **1.71V,** (*b*) **$-$79,000 cal.**]

13.9. (*a*) What is $E°$ for the cell

$$Sn \mid Sn^{2+} \parallel Ag^+ \mid Ag$$

(b) Write an equation for the cell reaction
(*c*) Which electrode is positive?
[**Ans.** (*a*) $+0.935$V, (*b*) $Sn + 2Ag^+ \rightarrow Sn^{2+} + 2Ag$, (*c*) Ag electrode.]

13.10. For the following standard cell

$$Ag \mid AgCl(s) \mid Cl^- \parallel Ag^+ \mid Ag$$

the anode reaction is $Ag + Cl^- \rightarrow AgCl + e^-$.
(*a*) Write the equation for the cell reaction
(*b*) Calculate $E°$ for the cell and ΔG for the cell reaction
[**Ans.** (*a*) $Ag^+ + Cl^- \rightarrow AgCl$, (*b*) $+0.5769$ V, -13.3 k. cal.]

13.11. What is the concentration of Cd^{2+} in the cell

$$Cd \mid Cd^{2+} (?M) \parallel Ni^{2+} (2.00M) \mid Ni$$

Given that the emf of this cell is 0.200 V? [**Ans.** 0.050 M.]

13.12. For the Cd^{2+}—Cd half-cell reaction, what would be the reduction potential at 25°C if the Cd^{2+} ion concentration was 0.01 M?
[**Ans.** $E°$ Cd^{2+}—Cd$= -0.402$ volt.]

13.13. Given the cell at 25°C,

$$Pb;\ Pb^{++}(a=1) \parallel Ag^+(a=1);\ Ag$$

(*a*) Calculate the voltage; (*b*) write the cell reaction; and (*c*) calculate the free energy change. [**Ans.** (*a*) 0.925 volt
(*b*) $\frac{1}{2}$ $Pb(s)+Ag^+(a=1)=\frac{1}{2}Pb^{++}(a=1)+Ag^+(s)$
(*c*) —21,330 cal.]

13.14. Given the cell at 25°,

$$Cd;\ Cd^{++}(a=1) \parallel I^-(a=1);\ I_2(s),\ Pt$$

(*a*) Write the cell reaction; (*b*) calculate E°; (*c*) calculate ΔG.
[**Ans.** (*a*) $Cd;\ Cd^{++}(a=1) \parallel I^-(a=1);\ I_2(s),\ Pt$
(*b*) 0.939 volt
(*c*) —43,300 cal.]

13.15. (*a*) Calculate the voltage of the following cell at 25°C;

$$Zn;\ Zn^{2+}(a=0.004) \parallel Cd^{2+}(a=0.2);\ Cd$$

(*b*) Write the cell reaction, (*c*) calculate the value of the free-energy change involved in the reaction.
[**Ans.** (*a*) 0.4398
(*b*) $Zn(s)+Cd^{2+}(a=0.2)=Zn^{2+}(a=0.0004)+Cd(s)$
(*c*) —20.287 cal.]

13.16. For the reaction

$$Zn(s)+2AgCl(s)=ZnCl_2(s)\ (0.555\ m)+2Ag(s)$$

$E_{0°C}=1.015$ volt while $\left(\frac{\partial E}{\partial T}\right)_P=-4.02\times10^{-4}$ volt/deg. Calculate ΔG, ΔH and ΔS of the reaction. [**Ans.** $\Delta S=-18.85$ eV.]

13.17. A cell contains two copper plates dipping in 0.05N and 0.005N solution of copper sulphate Calculate the emf of the cell neglecting the liquid junction potential. [**Ans.** 0.059 V.]

13.18. Calculate the emf of the cell at 18°C

$$Pt;\ H_2 \left| \ \frac{N}{10}\ HCl\ 1N\ KOH \ \right| H_2;\ Pt$$

Assume N/10 HCl as 90 per cent dissociated and 1 N-KOH as 75 per cent dissociated. Ionic product of water 1×10^{-14}. Neglect the liquid junction potential. [**Ans.** 0 747 V.]

13.19. Given the cell at 25°C

$$Pb \mid Pb^{2+}(1\ M) \parallel Ag^+(1\ M) \mid Ag$$

(*a*) Calculate the emf, (*b*) Calculate the free energy change $\Delta G°$.
[**Ans.** (*a*) 0.93 V, (b) —42.8 k.cal.]

13.20. How long could you run a motor requiring 15 ampere by the fuel cell reaction $CH_4+2O_2\rightarrow CO_2+2H_2O$ starting with a 50 litre tank of liquid methane (density 0.415 g/ml) and a 50 litre tank of liquid oxygen (density 1.149 g/ml)? Assume 100 per cent efficiency. [**Ans.** 535 days]

13.21. Given that the overall reaction for the lead storage cell is

$$Pb(s)+PbO_2(s)+2H_3O^++2HSO_4^-\rightarrow 2PbSO_4(s)+4H_2O$$

and that for the Edison cell is

$$Fe(s)+Ni_2O_3(s)+3H_2O\rightarrow Fe(OH)_2(s)+2Ni(OH)_2(s)$$

Calculate the relative efficiencies of those two cells in terms of coulombs produced per gram of reactants consumed. [**Ans.** 284 c/g and 701 c/g.]

13.22. A voltaic cell utilizes the reaction

$$Zn+Sn^{2+}\rightleftharpoons Zn^{2+}+Sn$$

What is the potential of the cell when
(*a*) (Conc. Sn^{2+})=1.0 M; (conc. Zn^{2+})=1.0 M?

(b) (Conc. Sn^{2+})=3.0 M; (Conc. Zn^{2+})=0.15 M?
(*c*) (Conc. Sn^{2+})=0.20 M; (Conc. Zn^{2+})=2.0 M?

[**Ans.** (*a*) +0.60 V, (b) 0.66 V, (*c*) 0.59 V.]

13.23. The reaction $M(s)+3N^+(aq.)\rightleftharpoons M^{3+}(aq.)+3N(s)$, is at equilibrium when $[N^+]=0\ 01$ M and $[M^{3+}]=0.004$ M. Calculate, *K*, *E*°, and △*G*° for the reaction. [**Ans.** $K=4\times10^3$, $E°=+0.071$ *V*; $\triangle G°=-4.0$ k.cal.]

13.24. Cobalt and nickel are notoriously similar in most of their chemistry. Find the equilibrium concentration of Ni^{2+} if 1.0 mole of Ni^{2+} is added to a 1.0 litre solution originally 2.00 M in a Co^{2+} (Ni and Co also present).

[**Ans.** +0.03 V for $Co+Ni^2\rightleftharpoons Co^{2+}+Ni$, $K=1.03$, $(Ni^{2+})=0.27$ M.]

13.25. Calculate the emf at 298 K of the following concentration cells
(*a*) Ag | $AgNO_3$ (aq. 0.01 mole kg^{-1}) ‖
$AgNO_3$ (aq., 0.1 mole kg^{-1}) | Ag
(*b*) Ag | $AgNO_3$ (aq., 0.01 mole kg^{-1})
$AgNO_3$ (aq., 0.1 mole kg^{-1}) | Ag
(*c*) Ag | AgCl(s), NaCl (aq., 0.1 mole kg^{-1}) ‖
NaCl (aq., 0.01 mole kg^{-1}), AgCl(s) | Ag
(*d*) Ag | AgCl(s), NaCl (aq., 0.1 mole kg^{-1}) ⋮
NaCl (aq., 0.01 mole kg^{-1}), AgCl(s) ¦ Ag
given the following activity coeffic ients and transport numbers:

		$r\pm$	t^+
0.01 mole kg^{-1}	$AgNO_3$	0.897	0.465
0.1 mole kg^{-1}	$AgNO_3$	0.734	0.468
0.01 mole kg^{-1}	NaCl	0.903	0.392
0.1 mole kg^{-1}	NaCl	0.778	0.385

(**Hint.** (*d*) $E_{cell}=2t+\frac{RT}{F}\ in\ \frac{a_{Cl^-}\text{ (in 0.1 mole kg}^{-1}\text{ NaCl)}}{a_{Cl^-}\text{ (in 0.01 mole kg}^{-1}\text{ NaCl)}}$

where t_+ is the transport number of Na^+. It is assumed that ${}_{\gamma}Na^+={}_{\gamma}Cl$)

[**Ans.** (*a*) 0.054 V, (*b*) 0.058 V, (*c*) 0.055 V, (*d*) 0 043 V.]

13.26. The emf of the cell
Hg | Hg_2Cl_2(s), KCl (aq., sat.) ‖ KCl (aq., 0.1 mole kg^{-1}), AgCl(s) | Ag is 0.047 V at 298 K. The potential of the saturated calomel electrode is 0.2415 V and the standard potential of the silver-silver chloride electrode is 0.225 V. Estimate an activity coefficient for the chloride ions in 0.1 mole kg^{-1} aqueous potassium chloride. [**Ans.** $\gamma_{Cl^-}=0.77$.]

13.27. Calculate the transport number of the copper ions in dilute copper sulphate solution, given that the emf at 298 K of the cell with transference.

Cu | $CuSO_4$ (aq., 0.001 mole kg^{-1}) $CuSO_4$ (aq., 0.01 mole kg^{-1}) | Cu

is 0.0268 V. The mean activity coefficients of 0.001 mole kg^{-1} and 0.01 mole kg^{-1} copper sulphate are 0.74 and 0.44 respectively.

[**Ans.** $t_{Cu^{2+}}=0.415$.]

13.28. Calculate the change in standard free energy at 298 K for the reaction.

$$Zn+Cu^{2+}\rightarrow Zn^{2+}+Cu$$

given that the standard electrode potential at 298 K for zinc and copper electrodes are—0.761 V and +0.340 V respectively.

[**Ans.** —212 kJ $mole^{-1}$.]

13.29. Calculate the solubility of AgBr in water at 298 K given the following standard electrode potentials:

Ag/Ag$^+$, $E^\circ_{298\text{ K}}=+0.799$ V

Ag/AgBr(s), Br$^-$, $E^\circ_{298\text{ K}}=+0.073$ V.

[**Ans.** Solubility$=7.3\times10^{-7}$ mole kg^{-1}.]

13.30. Determine the pH values for the titration curve obtained in the titration of 30.00 ml of 0.100 N benzoic acid, $HC_7H_5O_2$ with 0.100 N NaOH (*a*) after 10.00 ml of NaOH solution has been added, (*b*) after 30.00 ml of NaOH solution has been added, (*c*) after 40.00 ml of NaOH solution has been added. [**Ans.** (*a*) 3.92, (*b*) 8.46, (*c*) 12.16.]

13.31. Finally divided Ni is added to a solution in which the molality of Sn^{+2} is 0.1. What will be the activities of Ni^{2+} and Sn^{2+} when equilibrium is established? Assume that the molality is equal to activity for this reaction.

[**Ans.** $a_{\text{Ni}^{2+}}=0.10$, $a_{\text{Sn}^{2+}}=5.7\times10^{-5}$.]

13.32. The emf of the cell

H_2(g) buffer ‖ Normal calomel electrode

is 0.6885 volt at 40°C when the barometric pressure is 725 mm. What is the pH of the solution? [**Ans.** 6.60]

13.33. A 2.00 volt storage battery is used in an electrolysis in which a back emf of 1.45 volts is developed. If the resistance of the entire circuit is 10 ohms, (*a*) What is the magnitude of the current, and (*b*) What quantity of heat is generated by the current flow per faraday of electricity.

[**Ans.** (*a*) 3.055 amp (*b*) 12,690 cal.]

14

STRUCTURE OF ATOM

INTRODUCTION

Matter is composed of minute particles called atoms. The diameter of an atom is about an eight billionth of an inch. It is very difficult to imagine anything so small. John Dalton gave first theory of atom based on experimental data. The salient features of Dalton's atomic theory are:

(*i*) All matter is made up of tiny particles called atoms.

(*ii*) The atoms of a particular element have the same mass or at least an average mass characteristic of the element.

(*iii*) In chemical reactions only whole atoms participate.

(*iv*) Dalton regarded atoms as indivisible. The discrete nature of atom was established from Faraday's laws of electrolysis and the study of discharge through gases. From the study of various properties of cathode rays it appears probable that they consist of a stream of negatively charged particles called electrons. The rays emitted from the anode in the discharge tube are positively charged. These are called canal-rays and consist of particles called protons. J.J. Thomson determined e/m of electron and gave a value—1.76×10^8 coulombs/g. The charge on the electron was determined by R.A. Millikan by his famous oil drop method. The value of electric charge of an electron is -1.602×10^{-19} coulomb. The first model of atom was suggested by J.J. Thomson. He regarded atom as consisting of a positively charged substance distributed uniformly over the entire body of the atom. The negative electrons are embedded in this continuous positive charge. This model of the atom, which is known as the water-melon model, failed to explain the scattering of α-particles and the emission spectra of the elements. Rutherford studied the phenomenon of scattering of α-particles by thin sheets of metal. He observed that most of the α-particles passed through undeflected and only a few of them were scattered through large angles. He regarded atom as consisting of nucleus, where whole of the positive charge is concentrated and an extra-nuclear part in which electrons are revolving with a high velocity. This planetary model of the atom failed to explain the stability of the atom.

Line Spectra and Bohr Theory

When continuous light is passed through a prism it is dispersed into its components. This light when passed through the cells containing samples of atomic vapours, it is found that the light emitted is no longer continuous. The missing wavelengths can be measured by permitting the dispersed beam of light to fall on a photographic plate. This is known as absorption spectra. An absorption spectrum arises from the interaction of certain wavelengths of light with an atom. An emission spectrum arises from an excited atom emitting certain wavelengths of light corresponding to the emission of energy from the atom. The emission spectrum of the hydrogen gives rise to spectral series which are called Lyman series, Balmer series, Paschen series, Bracket series and Pfund series.

Niel Bohr suggested a model of the atom to explain the emission spectrum of the hydrogen atom. His model is based on the following assumptions:

(*i*) Electrons move in circular orbits around a central nucleus.

(*ii*) Only certain discrete orbits are permitted and the electrons radiate no energy when they are in these orbits.

(*iii*) A quantum of radiation is emitted or absorbed when an electron jumps from one orbit to another.

On the basis of these assumptions Bohr calculated the radius of hydrogen atom and obtained a value 0.529 Å. The energy of an electron in the hydrogen atom was calculated and the emission spectrum of hydrogen was successfully explained.

Bohr theory can be applied successfully to atoms or ions containing only one electron, i.e., hydrogen like atoms (He^+, Li^{2+}, Be^{3+}, etc.). The radius r of an atom from Bohr theory is given by the expression

$$r=\frac{n^2h^2}{4\pi^2mZe^2} \qquad \ldots (1)$$

where n is an integer and can take values 1, 2, 3 . . . etc. m is mass of one electron and e is the numerical value of the electron charge. Z is the nuclear charge, h is a constant called Planck's constant. It is a universal constant and has a value of 6.6×10^{-34} joule sec.

The total energy, E_{Total}, of an electron in an atom is given by the expression

$$E_{\text{Total}} = -\frac{2\pi^2 m Z^2 e^4}{h^2} \cdot \frac{1}{n^2} \qquad \ldots (2)$$

Wave Mechanics

Bohr theory assumed that electrons were moving in orbits about the nucleus. It explained the energies of the electron transitions in hydrogen and hydrogen-like atoms but not in any atom having more than one electron. The theory could not explain the different intensities of the spectral lines. This theory was improved by introducing the concept of elliptical orbits. Bohr theory still had fundamental inadequacies. Louis de Broglie proposed that, like light, a stream of electrons might have wave properties in addition to particle properties. He stated that there is an intimate relation between waves and particles. He gave the following relation between the wave and particle nature of electrons,

$$\lambda = \frac{h}{mv} \qquad \ldots (3)$$

where m is the mass of electron moving with a velocity v and λ is the wavelength of the light emitted. C.J. Davisson and L.H. Germer measured the wevelength of an electron and confirmed de Broglie's hypothesis.

Heisenberg noted that it is not possible to measure both the exact position of a small particle like electron and its exact momentum simultaneously. This is known as Heisenberg's uncertainty principle. If $\triangle q$ is uncertainty in the determination of position and $\triangle p$ is uncertainty in the determination of momentum, then

$$\triangle p \cdot \triangle q \geqslant h. \qquad \ldots (4)$$

Erwin Schrodinger in 1926, making use of de Broglie's idea of matter and waves developed a rigorous equation known as Schrodinger equation. This is a mathematical equation of second order, i.e.,

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \ldots (5)$$

where ∇^2 is known as Laplacian operator

$$\nabla^2 \approx \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \ldots (6)$$

where ψ is called the wave function, m is the mass of the electron E is the energy of the particle which is constant for the given value of λ. V is the potential energy of the particle of mass m, h is Planck's constant. The solutions of Schrodinger equation give ψ in terms of several variables one of which is the distance from the nucleus r. Once these solutions have been found it is possible to calculate ψ for each energy state at any point outside the nucleus. ψ^2 measures the probability of finding the electron in an infinitestimally small region of space situated at the point for which ψ^3 has been evaluated. Probability is used because it is impossible to determine the exact position of the electron. Charge cloud boundaries are used to enclose all the regions in which the chance of finding an electron is greater than 1 per cent. The solutions of Schrodinger equation are used to describe arrangement of electrons in atoms.

Particle in a box. In the case of a box, V is constant within the box (may be taken as zero), it is infinite at the wall of the box and thereafter. The solution of the Schrodinger equation in this case would be

$$\psi = A \sin \frac{n\pi x}{a} \qquad \ldots (7)$$

where n is an integer and can take values $n=1, 2, 3, \ldots$ etc., a is the side of the one dimensional box. $\psi^2(x)$ gives the probability of the particle being present at that x value, this being zero at the walls. On making the above substitution it is found that ψ is a solution if,

$$\epsilon = \frac{n^2h^2}{8ma^2} \qquad \ldots (8)$$

For a two-dimensional box

$$\epsilon = \frac{h^2}{8ma^2}(n^2x+n^2y) \qquad \ldots (9)$$

and for a three-dimensional box

$$\epsilon = \frac{h^2}{8ma^2}(n^2x+n^2y+n^2z) \qquad \ldots (10)$$

where the nT's independently take on the values 1, 2, 3, . . . etc.

Hydrogen-like atom. Schrodinger equation in the abbreviated form can be written as $H\psi=E\psi$.

The Hamiltonian operator H consists of a kinetic energy and a potential energy term. The kinetic energy term can be written as

$$-\frac{h^2}{8\pi^2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right) \qquad \ldots (11)$$

The potential energy term can be obtained by writing down all the various coulomb interations between electrons and between electrons and nuclei. In hydrogen-like atom there is a single electron and a nucleus of charge Z. Hence the potential energy of such a system would be $-\frac{Ze^2}{r}$. The wave equation can therefore be written

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-\frac{Ze^2\psi}{r}=E\psi \qquad \ldots (12)$$

The solution of this equation gives,

$$E=-\frac{2\pi^2 me^4Z^2}{n^2h^2}. \qquad \ldots (13)$$

The actual form of the functions ψ is complicated and usually expressed in polar coordinates. It can be expressed as a product of a function depending on radius alone, a function depending on ϕ alone, i.e.,

$$\psi(r, \theta, \phi) = R_{nl}(r)\ \Theta_{lm}\ (\Phi)\ \Phi(\phi) \qquad \ldots (14)$$

Here $R(r)$ goes through several nodes depending on the n and l values. Θ and Φ functions exhibit various lobes in their polar plot.

Quantum numbers. All the chemical and physical properties of an atom depend on the arrangement of its electrons, therefore quantum numbers, which are the solution of Schrodinger equation, provide useful chemical information.

Principal quantum number. It defines total energy of the electron and is designated by n. It can take integer values 1, 2, 3, . . . etc. The radius of the [charge cloud is proportional to n^2. A line enclosing the region in which the chance of finding a given electron is greater than one per cent gives the shape of charge cloud.

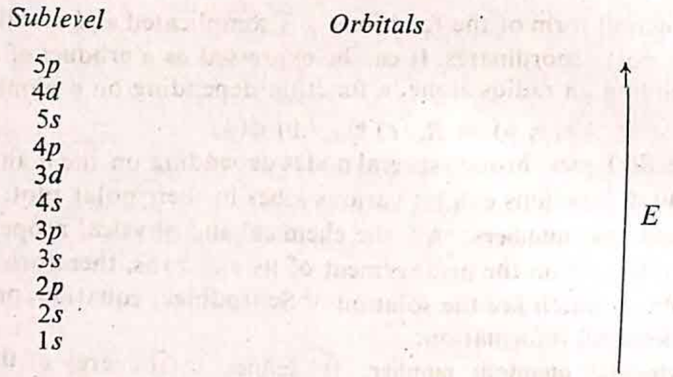
Azimuthal quantum number. It specifies the angular momentum of the electron. It is designated by l and can take values of 0, 1, 2, 3, . . . $n-1$.

Magnetic quantum number. It defines the possible orientations of the angular momentum in space with respect to some arbitrarily defined orientation. It is designated by m and can take values of $-l$, . . ., -2, -1, 0, $+2$, . . ., $+l$.

Spin quantum number. Spin quantum number does not come from the solution of the wave equation. It takes into account the spinning of the electron about its own axis as it moves about the nucleus. It can take values $+\frac{1}{2}$ or $-\frac{1}{2}$. The value of n the principal quantum number refers to the energy levels for $n=1, 2, \ldots$ these are known as K, L, M, N, . . . shells. In a level there are sublevels designated by small letters s, p, d, f . . . having angular momentum numbers, l of 0, 1, 2, 3 . . . respectively. The charge cloud distribution for electrons within a sublevel is called an orbital.

Pauli's exclusion principle. It states that no two electrons in the same atom can have the same set of four quantum numbers.

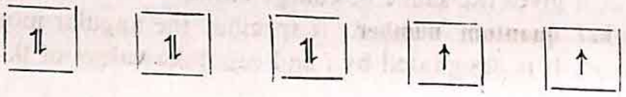
Hund's rule. This rule states that electrons will occupy the degenerate orbitals of a subshell singly with spins parallel until the subshell is half filled, and then successive electrons will begin to pair up in the already singly occupied orbitals. This rule is also known as rule of maximum multiplicity. In building up the electronic configuration of an atom, electrons are added first to orbitals in sublevels of lowest energy. The relative energy of the sublevels is shown below.



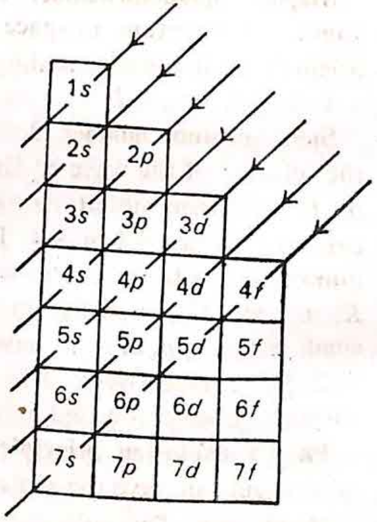
The electronic configuration of oxygen can be written as

$$O=8,\ 1s^2,\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1.$$

Another way of representing the configuration is



The ability to write electron configurations for neutral atoms and for positive and negative ions is fundamental to an understanding of chemistry. If one stacks up the various subshells as they occur in each main period of elements, the order of occupancy by electrons follows a diagonal pattern as shown below. The diagonal arrows indicate that the order in which the subshells are occupied by electrons is first the 1*s*, then the 2*s*, then the 2*p* followed by 3*s*, then the 3*p* followed by the 4*s*, then the 3*d*, 4*p* and 5*s* and so on.



In SI units the values of some important constants used in this chapter are:

(*i*) The speed of light in a vacuum is 2.997 × 10^8 ms^{-1}.

(*ii*) The Rydberg constant is $1.097 \times 10^7\ m^{-1}$.
(*iii*) The charge of an electron is 1.602×10^{-19} C.
(*iv*) The Planck constant is 6.626×10^{-34} Js.

Problem 14.1. Calculate the wavelength of light that has the energy 2.6×10^{-12} erg.

Solution. $E = h\nu = \dfrac{hc}{\lambda}$

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{6.63 \times 10^{-27}\ es \times 3.0 \times 10^{10}}{2.6 \times 10^{-12}\ e \times s}$$

$$\lambda = 7.6 \times 10^{-5}\ \text{cm}.$$

Problem 14.2. What is the energy of photons with wavelength 0.50 Å?

Solution. $E = h\nu$

$$E = hc/\lambda$$

$$E = \frac{6.63 \times 10^{-27}\ \text{erg sec} \times 3.0 \times 10^{10}}{0.50 \times 10^{-8}\ \text{cm}}\ \text{cm sec}^{-1}$$

$$E = 4.0 \times 10^{-8}\ \text{erg}.$$

Problem 14.3. An atom is known to absorb energy of 5.0×10^{-11} erg. In the spectrum of this atom, where will be a missing wavelength?

Solution. $E = h\nu$

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{6.62 \times 10^{-27}\ \text{erg sec } 3.0 \times 10^{10}}{5.0 \times 10^{-11}\ \text{erg.}}\ \frac{\text{cm}}{\text{sec.}} \times \frac{1\ \text{Å}}{10^{-8}\ \text{cm}}$$

$$\lambda = 400\ \text{Å}.$$

Problem 14.4. In the emission spectrum of hydrogen, the spectral series with *n* equal to three is called the Paschen series and is observed in the infrared region of the spectrum. Calculate the wave number for the limit of this series of lines.

Solution. The wave number of the individual lines obtained in the emission spectrum of hydrogen fits a mathematical series given by the formula

$$\bar{\nu} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$\bar{\nu}$ is the observed wave number, *R* is a constant called Rydberg's constant. m and n are integers, $m>n$. In each series the lines become closer together and reach a limit at m equal to infinity, i.e., $\frac{1}{m^2}=0$

$$\bar{\nu}=109{,}737\ \text{cm}^{-1}\left(\frac{1}{3^2}\right)$$
$$\bar{\nu}=109{,}737\ \text{cm}^{-1}\ (0.111)$$
$$\bar{\nu}=1.22\times10^{1}\ \text{cm}^{-1}.$$

Problem 14.5. If an electron drops back from the $n=2$ to $n=1$ energy level, what is the wave number that would be observed in the emission spectrum for the transition?

Solution. $\bar{\nu}=R\left(\frac{1}{n^2}-\frac{1}{m^2}\right)$

$$\bar{\nu}=109{,}737\left(\frac{1}{1^2}-\frac{1}{2^2}\right)\text{cm}^{-1}$$
$$\bar{\nu}=8.23\times10^{4}\ \text{cm}^{-1}.$$

Problem 14.6. Calculate the radius of the first allowed Bohr orbit for hydrogen atom.

Solution. $r=\frac{n^2h^2}{4\pi^2me^4}=\frac{1^2\times6.63\times10^{-27}\ \text{erg-sec.}}{4(3.14)^2(9.109\times10^{-28}\ \text{g})(4.8\times10^{-10})^4}$

$$r=0.529\times10^{-8}\ \text{cm}$$
$$r=0.529\ \text{Å}.$$

Problem 14.7. Calculate the energy of an electron in the first orbit of hydrogen.

Solution. $E=-\frac{e^2}{2r}$

$$E=\frac{-(4.8\times10^{-10}\ \text{esu})^2}{2(0.529\times10^{-8}\ \text{cm})}$$
$$E=-2.178\times10^{-11}\ \text{erg}.$$

Problem 14.8. Calculate the velocity of an electron in the first Bohr orbit of the hydrogen atom.

Solution. $v=n\left(\frac{h}{2\pi}\right)\frac{1}{m_er}$

$$n=1,\ r=0.529\times10^{-8}\ \text{cm}$$
$$v=\frac{1\times6.6256\times10^{-27}\ \text{erg-sec.}}{2(3.14)(9.109\times10^{-28}\ \text{g})(0.529\times10^{-8}\ \text{cm})}$$

Problem 14.9. If the electron of the hydrogen atom has been excited to a level corresponding to 10.2 electron volts, what is the wavelength of the line emitted when the atom returns to its ground state?

Solution. $\triangle E = E_2 - E_1$

$$\triangle E = h\nu$$

$$\triangle E = \frac{hc}{\lambda}$$

$$DE = 10.2 \text{ eV}$$

$$DE = 10.2 \times 1.6 \times 10^{-19} \text{ J}$$

$$\therefore \lambda = \frac{6.624 \times 10^{-34} \times 3 \times 10^{8} \text{ m}}{10.2 \times 1.6 \times 10^{-19}}$$

$$\lambda = \frac{6.624 \times 10^{-34} \times 3 \times 10^{8} \times 10^{9}}{10.2 \times 1.6 \times 10^{-19}} \text{ nm}$$

$$\lambda = 121.8 \text{ nm.}$$

Problem 14.10. A certain FM station broadcasts at a frequency of 89.7 Mc (89.7×10^{6} sec^{-1}). What is the wavelength of this transmission?

Solution. Since, $\lambda\nu = c$

Substituting the values of ν and c, we get,

$$\lambda\,(89.7 \times 10^{6} \text{ sec}^{-1}) = 3.00 \times 10^{10} \text{ cm sec}^{-1}$$

$$\lambda = \frac{3.0 \times 10^{10} \text{ cm sec}^{-1}}{89.7 \times 16^{6} \text{ sec}^{-1}}$$

$$\lambda = 3.34 \times 10^{2} \text{ cm}$$

$$\lambda = 3.34 \text{ m.}$$

Problem 14.11. Show that the ultraviolet line in the H atom spectrum corresponding to the transition 4 → 1, has (*a*) energy 294.0 k. cal. mole^{-1}, and (*b*) wavelength 973 Å. The energy of level 4 is —19.6 k. cal. mole^{-1} and that of level 1 is —313.6 k. cal. mole^{-1}.

Solution. (*a*) $\triangle E = E_{final} - E_{initial}$

$$\triangle E = -313.6 - (-19.6) \text{ k. cal. mole}^{-1}$$

$$\triangle E = -294.0 \text{ k. cal. mole}^{-1}.$$

This is the energy charge of the atom, the energy of the light quantum emitted has the positive value

$$\triangle E = +294.0 \text{ k. cal. mole}^{-1}$$

(*b* $\triangle E = h\nu$

$$\lambda\nu = c$$

$$\nu = \frac{c}{\lambda}$$

$$\therefore \quad \triangle E = hc/\lambda$$

$$\lambda = \frac{hc}{\triangle E}$$

$$\lambda = \frac{(9.54\times10^{-14}\ \text{k. cal mole}^{-1}\ \text{sec})\ (3\times10^{10}\ \text{cm sec}^{-1})}{294.0\ \text{k. cal. mole}^{-1}}$$

$$\lambda = 973\ \text{Å}.$$

Problem 14.12. What is the de Broglie wavelength of (*a*) a mass of 1 kg travelling at a speed of 1 cm s^{-1}, (*b*) the same travelling at 100 km s^{-1}, (*c*) a helium atom in a container at room temperature, and (*d*) an electron accelerated through a potential difference of 100 V, 1 kV, 100 kV?

Solution. Since, $\lambda = \dfrac{h}{p} = \dfrac{h}{mv}$

(*a*) $\lambda = (6.626\times10^{-34}\ \text{Js})/(10^{-3}\ \text{kg})\times(10^{-1}\ \text{ms}^{-1})$

$\lambda = 6.626\times10^{-29}\ \text{m}$

(*b*) $\lambda = (6.626\times10^{-34}\ \text{Js})/10^{-3}\ \text{kg})\times(10^{5}\ \text{ms}^{-1})$

$\lambda = 6.626\times10^{-36}\ \text{m}.$

(*c*) kinetic energy, $\frac{1}{2}mv^2 = \frac{3}{2}kT$

$\therefore$ $v = \sqrt{(3\,kT/m)}$

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{h}{m\sqrt{3\,kT/m}}$$

$$\lambda = \frac{h}{\sqrt{3\,kT\,m}}$$

$m = 4.00\times(1.66\times10^{-27}\ \text{kg})$

$m = 6.64\times10^{-27}\ \text{kg}$

$$\lambda = \frac{(6.626\times10^{-34}\ \text{Js})}{\sqrt{3\times6.64\times10^{-27}\ \text{kg}\times1.38\times10^{-23}\text{JK}^{-1}\times298\text{K})}}$$

$\lambda = 73\times10^{-12}\ \text{m}$

$\lambda = 73\ \text{pm}.$

(*d*) $\frac{1}{2}mv^2 = e\,\Delta\phi$

where $\Delta\phi$ is the potential difference

$\therefore$ $v = \sqrt{2\,e\,\Delta\phi/\text{m}}$

Since

$$\lambda = \frac{h}{mv}$$

$$\lambda = h/\sqrt{2\,me\,\Delta\phi}$$

$$\lambda = \frac{(6.626\times10^{-34}\ \text{Js})}{\sqrt{2\times9.11\times10^{-31}\ \text{kg}\times1.602\times10^{-19}\ \text{C}\times\Delta\Phi)}}$$

$\therefore$ $\text{J} = CV$

$\Delta\phi = 100\ V,\quad \lambda = (1.23\times10^{-9}\ \text{m})/\sqrt{100}$

$\lambda = 1.23 \times 10^{-10}$ m

$\lambda = 123$ pm.

$\Delta\phi = 1\ kV,\quad \lambda = (1.23 \times 10^{-9}\ \text{m})/\sqrt{10^3}$

$\lambda = 3.88 \times 10^{-11}$ m

$\lambda = 38.8$ pm.

$\Delta\phi = 100 kV,\quad \lambda = (1.23 \times 10^{-9}\ \text{m})/\sqrt{10^5}$

$\lambda = 3.88$ pm.

Problem 14.13. What is the degeneracy of the level of the hydrogen atom that has the energy (*a*) $-R_H$, (*b*) $-R_H/9$, (*c*) $-R_H/25$?

Solution. $E_n = -R_H/n^2$

(*a*) $E = -R_H$, $\therefore\ n = 1$ when $n = 1, l = 0$,

$m_e = 0$

$\therefore$ The level is degenerate.

(*b*) $E = -R_H/9$, $\therefore n = 3$ when $n = 3$, $\rho = 0, 1, 2$

when $l = 0$, $m_e = 0$ (1*s*-orbital)

when $l = 1$, $m_e = -1, 0, 1$ (3*d*-orbital)

when $l = 2$, $m_e = -2, -1, 0, 1, 2$ (5*d*-orbitals)

This is $1+3+5=9$ states in all. The degeneracy is 9.

(*c*) $E = -R_H/25$ $\therefore\ n = 5$, $\rho = 1, 2, 3, 4$

when $l = 0$, $m_e = 0$ (1*s*-orbital)

when $l = 1$, $m_e = -1, 0, 1$ (3*p*-orbital)

when $l = 2$, $m_e = -2, -1, 0, 1, 2$ (5*d*-orbital)

when $l = 3$, $m_e = -3, -2, -1, 0, 1, 2, 3$ (7*f*-orbitals)

when $l = 4$, $m_e = -4, -3, -2, -1, 0\ 1, 2, 3, 4$ (9*g*-orbitals)

That is $1+3+5+7+9=25$ states in all. The degeneracy is 9 . . . .

Problem. 14.14. Calculate λ for an electron moving with 0.1 G using resting mass $m_e = 9.109534 \times 10^{-31}$ kg as the mass.

Solution. $\lambda = \dfrac{h}{mv}$

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{Js}}{(9.11 \times 10^{-31}\ \text{kg})(0.1)(3.00 \times 10^{-8}\ \text{ms}^{-1})}$$

$\lambda = 2.42 \times 10^{-11}$ m.

Problem 14.15. The de Broglie wavelength of a particle is given by $\lambda = h/p$ where p denotes the momentum of the particle. Show that a Bohr orbit for a hydrogen-like atom has a circumference that is an integral multiple of de Broglie wavelengths of an electron of that momentum.

Solution. According to Bohr angular momentum of an electron is quantized, i.e., $mvr = \dfrac{nh}{2\pi}$ . . . (1)

n is an integer. This equation may be written as,

$$2\pi r = n.\frac{h}{mv} \qquad \ldots (2)$$

$$2\pi r = n.\frac{h}{p} \qquad \ldots (3)$$

since $$p = mv.$$

Equation (3) can be written as using de Broglie's relation

$$2\pi r = n\lambda \qquad \ldots (4)$$

Hence the Bohr orbit for a hydrogen-like atom has a circumference that is an integral multiple of de Broglie wavelengths of an electron of that momentum.

Problem 14.16. The minimum energy necessary to overcome the attractive force between the electron and the surface for silver metal is 7.52×10^{-12} erg. What will be the maximum kinetic energy of the electrons ejected from silver which is being irradiated with ultraviolet light having a wavelength 360 Å?

Solution. $E = h\nu_0 = 7.52 \times 10^{-2}$ erg

$$\frac{1}{2}mv^2 = h - h_0$$

$$\frac{1}{2}mv^2 = \frac{hc}{\lambda} - h\nu_0$$

$$\frac{1}{2}mv^2 = \frac{(6.63 \times 10^{-27} \text{ erg sec})\,(3 \times 10^{10} \text{ cm sec}^{-1})}{3.60 \times 10^{-10}}$$

$$\frac{1}{2}mv^2 = 7.52 \times 10^{-12} \text{ erg}$$

$$\frac{1}{2}mv^2 = 4.77 \times 10^{-11} \text{ erg.}$$

Problem 14.17. The eigen function for a 1s electron of a hydrogen like atom is given by $\psi = k.e.\frac{-Ze}{a^{o}}$ where k is a constant and a° is the radius of the first Bohr orbit for hydrogen. Show that the radius at which there is a maximum probability of finding a 1s electron is just $r_{max} = a^{\circ}/Z$.

Solution. The probability, P, of finding an electron in unit element of volume at a distance r is given by ψ^2 and the probability of finding the electron at a distance r is given by $4\pi r^2\psi^2$.

This is denoted by P, given by

$$P = kr^2 e - \frac{2Zr}{a^{o}}$$

$$\frac{dP}{dr}=k\left[2re^{-2Zr/a^0}-r^2 2\left(\frac{Z}{a_o}\right)e^{-2Zr/a_0}\right]$$

$$=k.2re^{-2Zr/a_0}\left(1-\frac{Zr}{a_o}\right)$$

The solution therefore is, $\frac{Zr}{a_o}=1$

or $$r_{max}=\frac{a_o}{Z}.$$ **Ans.**

Problem 14.18. Obtain the expectation values of x, x^2, p and px^2 for the particle in the box. Calculate the value of $(\triangle x)_{rms}$. $(\triangle px)_{rms}$. Is this in accordance with Heisenberg's uncertainty principle?

Solution. The physical quantity and the corresponding operators are

Physical quantity	x	x^2	px	px^2
Operator	$X=x$	$x^2=x^2$	$\frac{h}{2\pi_2}\cdot\left(\frac{d}{dx}\right)$	$-\frac{h}{4\pi^2}\left(\frac{d^2}{dx^2}\right)$
Expectation value	$\overline{x}$	$\overline{x}^2$,	px	$p\overline{x}^2$

(*i*) Calculation of $\overline{x}$

$$\overline{x}=\frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi x}{a}\right)dx.$$

$$\overline{x}=\frac{2a}{(n\pi x)^2}\int_0^{n\pi}\beta\sin\beta.\,d\beta$$

$$\overline{x}=\frac{2a}{(n\pi)^2}\left[\frac{\beta^2}{4}-\frac{\beta\sin 2\beta}{4}-\frac{\cos 2\beta}{8}\right]_0^{n\pi}$$

$$\overline{x}=\frac{a}{2}$$

(*ii*) Calculation of $\overline{x}^2$:

$$\overline{x}^2=\frac{2}{a}\int_0^a x^2\sin^2\left(\frac{n\pi x}{a}\right)\partial x$$

$$\overline{x}^2=\frac{2a^2}{(n\pi)^3}\left[\frac{\beta^3}{6}-\left(\frac{\beta^2}{4}-\frac{1}{8}\right)\sin 2\beta-\beta\,\frac{\cos 2\beta}{4}\right]_0^{n\pi}$$

$$\overline{x}^2=\frac{a^2}{3}\left(1-\frac{3}{2n^2\pi^2}\right)$$

(*iii*) Calculation of $\bar{p}_x$

$$\bar{p}_x=\frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\left(\frac{h}{2\pi i}\ \frac{d}{dx}\right)\sin\left(\frac{n\pi x}{a}\right)dx$$

$$\bar{p}_x=\frac{nh\pi}{a^2\pi i}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cos\left(\frac{n\pi x}{a}\right)dx$$

$$\bar{p}_x=0$$

This corresponds to the classical picture of a particle moving back and forth with constant velocity. This gives an average momentum equal to zero.

(*iv*) Calculation of $\bar{p}_x{}^2$

$$p_x{}^2=\frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\left(-\frac{h^2}{4\pi^2}\frac{d^2}{dx^2}\right)\sin\left(\frac{n\pi x}{a}\right)dx$$

$$p_x{}^2=\frac{2n^2\pi^2h^2}{a^3 4\pi^2}\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx$$

$$p_x{}^2=\frac{n^2h^2}{4a^2}$$

$$p_x{}^2=2mE$$

The Heisenberg uncertainty relation:

(*v*) Let x stand for the result of a single measurement of the system. Then the deviation of this measurement from the averge is

$$\Delta x=x-\bar{x};$$

$$(\Delta x)^2=(x-\bar{x})^2$$

$$\overline{(\Delta x)^2}=\overline{(x-\bar{x})^2}$$

$$=\bar{x}^{-2}-\bar{x}^2$$

$$\therefore\quad \sqrt{\overline{(\Delta x^2)}}=(\Delta x)_{rms}=\sqrt{\bar{x}^{-2}-\bar{x}^2}$$

Thus $$(\Delta x)_{rms}=\left[\frac{a^3}{3}\left(1-\frac{3}{2n^2\pi^2}\right)-\frac{a^2}{2}\right]^{1/2}$$

$$(\Delta x)_{rms}\approx\left(\frac{1}{6}(2a^3-3a^2)\right)^{1/2}$$

$$(\Delta x)_{rms}=\sqrt{\frac{2}{3}}$$

$$(\Delta x)_{rms}=0.819.$$

$$\therefore\quad (\Delta p_x)_{rms}=\left(\frac{n^2h^2}{4a^2}\right)^{1/2}$$

$$(\triangle p_x)_{rms}=\frac{nh}{2a}$$

$$(\triangle p_x)_{rms}=\frac{nh}{4}$$

$$\therefore \quad (\triangle x)_{rms}\cdot(\triangle p_x)_{rms}$$

$$=0.819\times\frac{nh}{4}$$

$$=0.205\ nh$$

$$=\sim h.$$

The uncertainties in the position and momentum are thus in accordance with Heisenberg's principle which requires that

$$\triangle x \triangle p_x \geqslant h.$$

Problem 14.19. What is the electron configuration for (*a*) Nitrogen, (*b*) sodium, (*c*) aluminium, and (*d*) chromium?

Solution. (*a*) Nitrogen is element of atomic number 7, its configuration is

$1s^2$, $2s^2$ $2p^3$ $(2+2+3=7)$

(*b*) Sodium is element of atomic number 11

$1s^2$, $2s^2$ $2p^6$, $3s^1$ $(2+2+6+1=11)$

(*c*) Aluminium is element of atomic number 13.

$1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^1$ $(2+2+6+2+1=13)$

(*d*) Chromium is element of atomic number 24.

Its configuration is expected to be,

$1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^4$, $4s^2$

However the actual configuration is

$1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^5$, $4s^1$ $(2+2+6+2+6+5+1=24)$

This is because two half filled subshells, $3d^5$ and $4s^1$ is a more stable arrangement than one partially filled, $3d^4$ and one completely filled, $4s^2$.

Problem 14.20. Write the electron configuration for the element with atomic number 118.

Solution.

$1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^{10}$, $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$, $5s^2$ $5p^6$ $5d^{10}$ $5f^{14}$, $6s^2$ $6p^6$ $6d^{10}$, $7s^2$ $7p^6$.

Problem 14.21. Which of the following transitions are allowed in the normal electronic spectrum of an atom: (*a*) $2s \rightarrow 1s$, (*b*) $2p \rightarrow 1s$, (*c*) $3d \rightarrow 2p$, (*d*) $5d \rightarrow 3s$, (*e*) $3p \rightarrow 3s$?

Solution. $\triangle l=\pm 1$, $\triangle n=$any integer

(*a*) $2s \rightarrow 1s$ $\triangle l=0$ $\therefore$ forbidden

(*b*) $2p \rightarrow 1s$ $\triangle l=-1$, $\triangle n=1$ $\therefore$ allowed

(*c*) $3d \rightarrow 2p$ $\triangle l=-1$, $\triangle n=1$ $\therefore$ allowed (*d*) $5d \rightarrow 3s$ $\quad \triangle l=2 \quad \therefore$ forbidden

(*e*) $5p \rightarrow 3s$ $\quad \triangle l=1, \triangle n=2 \quad \therefore$ allowed.

Problem 14.22. A hydrogen-like $1s$-orbital in an atom of atomic number Z is the exponential function $\psi_{1s}(r)=(Z/\pi a_o^3)^{1/2} \exp(-Zr/a_o)$. Form the radial distribution function and derive an expression for the most probable distance of the electron from the nucleus. What is its value in the case of (*a*) helium, (*b*) fluorine?

Solution. $\Psi_{1s}(r)=\left(\frac{Z}{\pi a_o^3}\right)^{\frac{1}{2}} \exp\left(\frac{-Zr}{a_o}\right) \qquad a_o=53 \text{ pm}$

Radial distribution function (RDF)

$$=4\pi r^2\Psi^2_{1s}(r)=4\pi r^2\left(\frac{Z}{\pi a_o}\right) \exp\left(\frac{-2Zr}{a_o}\right)$$

The most probable distance is the value of r for which the radial distribution function is maximum

$$\frac{d}{dr}(\text{RDF})= 8\pi r\left(\frac{Z}{\pi a_o}\right)e^{-2Zr/a_o}-8\pi\left(\frac{Z}{a_o}\right)r^2\left(\frac{Z}{\pi a_o}\right)e^{-2Zr/a_o}=0$$

$\therefore$ at $r=r^*$

$\therefore \quad 1=\frac{Zr^*}{a_o} \qquad$ or $\quad r^*=a_o/Z$

(*a*) $Z=2; \quad r^*=a_o/2=26$ pm

(*b*) $Z=9; \quad r^*=a_o/9=5.9$ pm.

Problem 14.23. What values of J may arise in the following terms: ^1S, ^2P, ^3P, ^3D, ^2D, ^1D, ^4D? How many states occur in each level?

Solution. Since $J=L+S, L+S-1, \ldots \mid L-S \mid$

^1S; $L=0$ $S=0$ $\therefore J=0$, i.e. $^1S_0$; $2J+1=1 \therefore$ 1 state

^2P; $L=1$ $S=\frac{1}{2}$ $\therefore J=\frac{3}{2}, \frac{1}{2}$, i.e., $^2P_{3/2}$, $^2P_{1/2}$ with 4, 2 states respectively.

^3P; $L=1, S=1 \therefore J=2, 1, 0$ i.e., $^3P_2$, $^3P_1$, $^3P_0$ with 5, 3, 1 states respectively.

^3D; $L=2, S=1 \therefore J=3, 2, 1$ i.e., $^3D_3$, $^3D_2$, $^3D_1$ with 7, 5, 3 states respectively.

^2D; $L=2, S=\frac{1}{2} \therefore J=\frac{5}{2}, \frac{3}{2}$, i.e., $^2D_{5/2}$, $^2D_{3/2}$ with 6, 4 states respectively.

^1D; $L=2, S=0 \therefore J=2$, i.e., $^1D_2$ with 5 states.

^4D; $L=2$, $S=\frac{3}{2}$, $\therefore J=\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$, i.e., $^4D_{7/2}$, $^4D_{5/2}$, $^4D_{3/2}$, $^4D_{1/2}$ with 8, 6, 4, 2 states respectively.

EXERCISES

14.1. Fill in the blanks:

(*i*) The electron is . . . charged particle with a mass . . . g.

(*ii*) The proton is . . . charged particle with a mass . . . g.

(*iii*) The nucleus is made up of . . . and . . .

(*iv*) In a hydrogen atom consisting of just one proton and one electron, the greatest proportion by weight is accounted for by the . . . (electron, proton).

[**Ans.** (*i*) negatively, 9.11×10^{-28} g; (*ii*) positively, 1.673×10^{-24} g; (*iii*) neutron, proton; (*iv*) proton.]

14.2. If an iron atom is spherical in shape and its volume is 1.8×10^{-23} c.c., what is the radius of an iron atom? [**Ans** 1.41×10^{-8} cm.]

14.3. Compare the emission spectra of atomic hydrogen and deuterium. Assume $m_e=9.109534\times10^{-31}$ kg and $m_{\text{nucleus}}=1.6726485\times10^{-27}$ kg for H and 3.343398×10^{-27} kg for D.

[**Ans.** R=109,677.59 cm^{-1} for H and 109,707.43 cm^{-1} for D, giving slightly higher values of $\bar{\nu}$ and slightly lower values of λ for D.]

14.4. Iron has an atomic weight of 55.8 and a density of 7.87 g/c.c. Calculate the volume occupied by each iron atom. [**Ans.** 1.8×10^{-23} c.c./atom.]

14.5. The nucleus of platinum atom has a radius of 5.0×10^{-4} cm. Platinum has an atomic weight of 195.2 and a density of 21.4 g/c.c. If a platinum atom is spherical in shape, how many times larger is the radius of platinum atom than the radius of the nucleus? [**Ans.** 3.1×10^{5}.]

14.6. The frequency of a wave of light is 1.0×10^{6} sec^{-1}. What is the wavelength for this wave? [**Ans.** 3.0×10^{4} cm.]

14.7. If the wavelength of green light is about 5000 Å, what is its frequency? [**Ans.** 6.0×10^{14} sec^{-1}.]

14.8. In a photoelectric effect experiment, light of frequency 1×10^{16} sec^{-1} yielded electrons with maximum kinetic energy 5.0×10^{-11} erg. Calculate ν_0 for the metal. [**Ans.** 2.5×10^{15} sec^{-1}.]

14.9. When a certain metal was irradiated with light having a frequency of 3.0×10^{16} sec^{-1}. The photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light having a frequency of 2.0×10^{16} sec^{-1}. Calculate ν_0 for the metal. [**Ans.** 1.0×10^{16} sec^{-1}.]

14.10. Which of the following statements concerning the function of the two quantum number are correct?

(*i*) l determines the size of an orbital.

(*ii*) n determines the shape of an orbital.

(*iii*) n determines the size of an orbital.

(*iv*) l determines the shape of an orbital.

(*v*) n determines the number of lobes of electron density in an orbital.

[**Ans.** (*iii*) and (*iv*) are correct.]

14.11. Which of the following rules must be adhered to in the Aufbau process?

(*i*) An orbital can accommodate a maximum of two electrons. To do so the electrons must be of opposite spins.

(*ii*) Electrons have to be fed into the orbitals in order of increasing energy.

(*iii*) Each set of orbitals of the same energy has to be completely filled before proceeding to the next orbital or set of orbitals.

(*iv*) Whenever electrons are added to orbitals of the same energy if possible, each orbital is allocated one electron before any pairing occurs.

(*v*) Whenever electrons are allocated singly to separate orbitals of the same energy, the electrons must all have the same spin. [**Ans.** (*iv*).]

14.12. Match the terms on the left with the definition on the right:

A. Pauli exclusion principle	(*a*) the wave function squared.
B. Schrödinger equation	(*b*) a solution of the wave equation.
C. Hund's rule	(*c*) no two electrons may have the same four quantum numbers.
D. Wave function	(*d*) in orbitals of equivalent energy electron spins remain unpaired, if possible.
E. Probability	(*e*) relation of energy to wave properties.
F. Uncertainty principle	(*f*) the position and velocity of an electron may not be measured simultaneously and exactly.

[**Ans.** A (*c*), B (*e*), C (*d*), D (*b*), E (*a*) F (*f*).]

14.13. Match the terms on the left with the symbols on the right:

A. Wave nature of matter	(*a*) Ψ
B. Uncertainty principle	(*b*) $\lambda = h/p$
C. Probability	(*c*) $(\Delta p)(\Delta x) \geqslant h/4\pi$
D. Wave function	(*d*) $N^2 e^{-2r}$
F. Probability density	(*e*) Ψ^2

[**Ans.** A (*b*), B (*c*), C (*e*), D (*a*), E (*d*).]

14.14. The work function which is the maximum energy required to remove an electron from a substance, is related to

(*a*) the wave number.
(*b*) the angular momentum.
(*c*) the threshold frequency.
(*d*) the quantum number.
(*e*) the frequency. [**Ans.** (*c*) the threshold frequency.]

14.15. The diameter of earth is about 8,000 kilometres. Imagine the situation in which only the nuclei of all the atoms in the earth were piled together

(*a*) How high a sphere would you have?
(*b*) It is impossible to perform this imaginary feat because of the tremendous forces of electrical repulsion that would be produced. Explain.

[**Ans.** (*a*) The diameter of the nucleus is 1/10,000 the diameter of the atom. So, if the bare nuclei were piled together, the earth would be a sphere 0.8 kilometre in diameter.

(*b*) There would be no negative electric charges to offset the repulsion of all the positively charged nuclei.]

14.16. Select the term best associated with each definition, description or specific examples.

Terms: (A) Planck's constant (B) discontinuous spectra (C) ground state (D) Bohr atom (E) quantum mechanics.

(*a*) for the carbon atom, it may be represented by $1s^2, 2s^2, 2p_x{}^1, 2p_y{}^1$.
(*b*) application of wave characteristics to certain properties of matter.
(*c*) experimental evidence for quantized energies of electrons in atoms.
(*d*) model suggesting quantized orbits for electrons in atoms.
(*e*) equal to $E\lambda$ divided by c.

[**Ans.** *a* (C), *b* (E), *c* (B), *d* (D), *e* (A).

14.17. Select the terms, best associated with each definition, description or specific example.

Terms: (A) continuous spectrum (B) electron diffration (C) empirical (D) exact state (E) isoelectronics (F) kinetic energy (G) momentum (H) orbit (I) quantum numbers (J) sublevels.

(*a*) characterised by energy greater than that of the ground state.
(*b*) closed trajectory around a reference point.
(*c*) designations of electron characteristics contributing to an overall energy state.
(*d*) 2*s*.
(*e*) light from an incandescent source.
(*f*) derived from experimental rather than theoretical considerations.
(*g*) evidence for wave properties of electrons.
(*h*) evidence for wave properties of electrons such as Li and He.
(*i*) *mv*.
(*j*) $\frac{1}{2}mv^2$.

[**Ans.** *a* (D), *b* (H), *c* (I), *d* (J) *e* (A), *f* (C), *g* (D), *h* (E), *i* (G) & *j* (F).]

14.18. Select the term best associated with each definition, or specific example.

Terms: (A) Bohr model (B) comptom scattering (C) discontinuous spectra (D) ground state (E) isoelectronic (F) node (G) orbital (H) potential energy (I) quantum numbers (J) rest mass.

(*a*) experimental evidence for quantized energies of electrons in atoms.
(*b*) experimental evidence for particle properties of light.
(*c*) model suggesting quantized orbits in atoms.
(*d*) 2*s*.
(*e*) a region of zero probability.
(*f*) for the electrostatic system represented by the hydrogen atom, this term is $\frac{-e^2}{r}$.
(*g*) He, Li^+, H^-.
(*h*) for the electronic system of the Li atom, it may be represented by $1s^2$, $2s^1$.
(*i*) suggested to be zero for a photon.
(*j*) designated by characteristic values for the symbol *n*, *l*, *m* and *s*.

[**Ans.** *a* (C), *b* (B), *c* (A), *d* (G), *e* (F), *f* (H), *g* (E), *h* (D), *i* (J), *j* (I).]

14.19. Calculate the ionization potential (in calories per atom) for the hydrogen atom (corresponding to a transition for $n = 1$ to $n = 0$ that is, from $\frac{1}{n^2} = 1$ to $\frac{1}{n^2} = 0$). The experimental value for the ionization potential of the hydrogen atom is 13.6 electron volts per atom. Compare this with the calculated value. [**Ans.** 5.2×10^{-19} (13.7 eV.]

14.20. Calculate the wavelength in the hydrogen spectrum, in angstroms, corresponding to an electron transition from $n=7$ to $n=2$. $R=1.098 \times 10^{-3}$ A^{-1}.
[**Ans.** 3970 Å.]

14.21. Find the most probable radius at which an electron will be found when it occupies a 1*s* orbital of an atom with atomic number *Z*, and tabulate the values for the first row of the periodic table.
[**Ans.** H 53; He 26; Li 18; Be 11; B 11; C 8.8; N 7.6; O 6.6; F 5.9; Ne 5.3.]

14.22. A series of lines in the spectrum of atomic hydrogen lies at the wavelengths

656.46 nm, 486.27 nm, 434.17 nm and 410.29 nm. What is the wavelength of the next line in the series? What is the energy required to ionise the hydrogen atom? [Ans. 397.13 nm; 3.40 eV.]

14.23. What is the ratio between the coefficients of spontaneous and stimulated emission for light with a wavelength of 6000Å and for the microwave radiation with a wavelength of 3 cm?

[**Ans.** 6000Å, $\left(\frac{A}{B}\right)=7.7076\times10^{-13}$ cgs units 3 cm, $\left(\frac{A}{B}\right)=6.166\times10^{-27}$ cgs units.]

14.24. The work function W is the potential barrier that an electron must pass in order to be able to leave a metal. If W is 2eV, what is the value of the frequency ν_0 and wavelength λ_0 of the light that we must shine to begin to observe the photoelectric effect.

[**Ans.** $\nu_0=4.837\times10^{14}\ s^{-1}$, $\lambda_0=6197.7$Å.]

14.25. If it takes approximately 1 erg of energy for a fly to lift off from a table top how many flies could get air borne by a Avogadro's number of photons of the yellow sodium light of wavelength 5800Å? [**Ans.** 2.0×10^{12} flies.]

14.26. The ionization energy of potassium is 425 kJ/mole. What must be the minimum frequency of a photon that can affect its ionization?

[**Ans.** 1.06×10^{15} sec^{-1}.]

14.27. Match the following:

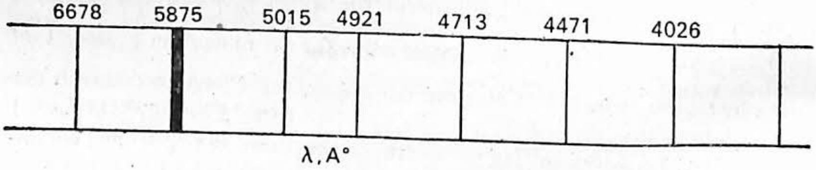
(*a*) Frequency	(1) 4863Å
(*b*) (Wavelength)×frequency	(2) c/λ
(*c*) Energy	(3) $h\nu$
(*d*) Infra-red	(4) 3×10^{10} cm
	(5) Δn
	(6) 10,000 Å.

[**Ans.** (*a*) 2, (*b*) 4, (*c*) 3, (*d*) 6.]

14.28. What is the energy of light having wavelength 100Å expressed in kilocalories per mole? (*b*) How does this compare with the amount of energy required to ionize H atoms? (*c*) What effect would a light quantum of this wavelength have if it collided with a hydrogen atom?

[**Ans.** (*a*) 2.86×10^3 k.cal/mole^{-1}, (*b*) larger than IE, (*c*) it would ionize the H atom.]

14.29. The emission spectrum of ${}^4_2$He is shown below



The wavelengths are given in Å.

(*a*) Indicate the emission lines of highest and lowest energy.

(*b*) Calculate the frequency of the two lines in (*a*).

(*c*) Assume that the figure shown is a photographic record of the spectum. Would the lines be bright against a dark background or dark against a light background? Why?

[**Ans.** (*a*) Highest energy, 4026Å, lowest energy 6678 Å; (*b*) 7.447×10^{14}Hz and $4.489\times^{14}$ Hz; (*c*) Bright against dark background. This is because the emitted light strikes exposed film only at lines.]

14.30. The following are the characteristic X-ray wavelengths for some metals. Rb, 0.93Å; Mg, 9.87Å; Cr, 2.29Å, Ca, 3.35Å. (*a*) Calculate the energy level differences in these atoms indicated by the emission of X-rays. (*b*) What orbitals might be involved in these transitions?

[**Ans.** (*a*) Rb, 2.1×10^{-8} ergs; Mg, 2.01×10^{-0} ergs; Cr, 8.7×10^{-9} ergs; Ca 5.9×10^{-9} ergs; (*b*) 2*s* to 1*s*.]

14.31. Using the hydrogen atom as the model (*a*) Calculate the energy when the principal quantum number of its electron is 6, and (*b*) calculate the work done in kJ/mole required to ionize a hydrogen atom whose electron was originally in the $n=2$ level.

[**Ans.** (*a*) -6.1×10^{-13} ergs/atom, (*b*) 3.3×10^{2} kJ/mole.]

14.32. The solution of Schrödinger equation for an electron in the ground state of the hydrogen atom is

$$\varphi_{1s}=\frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}$$

where r is the distance from the nucleus and a_0 is 0.529×10^{-8} cm. The probability of finding an electron at any point in space is proportional to $|\Psi'|^2$. Show that the maximum probability of finding the electron in the 1*s* orbital of hydrogen occurs at $r=a_0$.

14.33. The ionization potential of the outer electron of sodium is 0.2 atomic energy units. Assuming the sodium atom as a hydrogen like kernel plus the outer electron. Calculate the effective nuclear charge seen by that electron. [**Ans.** 1.9.]

(**Hint.** For sodium atom $n=3$ and the ionization energy would be $\frac{13.6}{9}$ or 1.5 eV.)

14.34. The energy of a particle in a one dimensional box is given by $\varepsilon=\frac{h^2}{8ma^2}$. Show that the product of the momentum p of the particle a is of the order of magnitude of h. The relativistic effects may be neglected.

14.35. A cubic box of side 10 Å contains 8 electrons. Using the concept of simple particle in a box, calculate $\Delta\varepsilon$ for the first excited state of the system.

[**Ans.** 1.13 eV.]

14.36. An electron confined to a one dimensional box 1.4 Å in length has a ground-state energy corresponding to light of wavelength about 700 Å. Benzene, as a rough approximation, may be considered to be a two dimensional box that encompasses the regular hexagonal shape. The C—C bond length in benzene is 1.4Å so the side of the box would be 2.8Å. Estimate the wavelength for transition from ground state to excited state of benzene assuming it is just the π-bonding electrons that are involved.

[**Ans.** 930 Å]

14.37. A linear conjugated system, that is, —C=C—C=C—C=, contains P carbon atoms in the chain; the average C—C distance may be taken to be 1.5Å. If $\Delta\varepsilon$ for the transition from the ground to the first excited state is 2 eV, show what the value of P must be, according to the particle in a box-treatment. [**Ans.** 9.0]

14.38. A hydrogen like wave function Ψ_{nlm} is of the form Ψ_{nlm} = (Const.) $r^4 \sin^4\theta \sin^4\varphi$. Calculate the values of n, l and m.

[Ans. $n = 5$, $l = 4$, $m = 4$.]

14.39. Evaluate the normalization constant for a system of non-interacting particles moving along the x-axis if there are s_0 particles per unit length l. The value of l is chosen in such a way that the $\cos l = 0$.

$$\left[\text{Ans. } \varphi\ (n) = \sqrt{2s_0} \sin\left(\frac{n\pi n}{l}\right)\right]$$

14.40. Calculate the mean position $\bar{x}$, $\bar{x}^2$, the mean momentum $\bar{p}_n$ and the mean kinetic energy E_{kin} of the quantum state with state function,

$$x = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

where a is a constant having the dimensions of length.

$$\left[\text{Ans. } \bar{x} = \frac{a}{2};\ \bar{x}^2 = \frac{a^2}{3}\left(1 - \frac{3}{2\pi^2}\right);\ p_x = 0,\ E_{kin} = \frac{h^2}{8ma^2}.\right]$$

14.41. What group will the elements with these electron configurations occupy in the periodic table?

(*a*) $1s^2, 2s^2\,2p^1$

(*b*) $1s^2, 2s^2\,2p^6, 3s^2$

(*c*) $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^3, 4s^2$

(*d*) $1s^2, 2s^2\,2p^6, 3s^2\,3p^6$.

[Ans. (*a*) Group IIIA, (*b*) Group IIA, (*c*) Group VB, (*d*) Zero group.]

14.42. The electron configurations for some elements are given below. What are the quantum numbers n and l for the outermost electrons in each element?

(*a*) Li $1s^2, 2s^1$

(*b*) Cl, $1s^2, 2s^2\,2p^6, 3s^2\,3p^5$

(*c*) Zn, $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2$

(*d*) Fe, $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^6, 4s^2$.

[Ans. (*a*) $n=2$, $l=0$; (*b*) $n=3$, $l=1$; (*c*) $n=4$, $l=0$; (*d*) $n=4$, $l=0$.]

14.43. What shell and subshell are represented by following values of n and l?

(*a*) $n=3$, $l=1$; (*b*) $n=4$, $l=3$; (*c*) $n=7$, $l=0$.

[Ans. (*a*) 3*p*, (*b*) 4*f*, (*c*) 7*s*.]

14.44. Write the electron configuration of Ni^{2+} ion.

[Ans. $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^8$.]

14.45. Write the electron configurations for the following ions:

(*a*) Cl^-, (*b*) Ca^{2+}, (*c*) Fe^{2+}, (*d*) Cr^{3+}, (*e*) N^{3-}.

[Ans. (*a*) $1s^2, 2s^2\,2p^6, 3s^2\,3p^6$ (*b*) $1s^2, 2s^2\,2p^6, 3s^2\,3p^6$ (*c*) $1s^2\,2s^2\,2p^6, 3s^2\,3p^6, 3d^6$, (*d*) $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^3$ (*e*) $1s^2, 2s^2\,2p^6$.]

14.46. Identify the first element appearing in the periodic table which has

(*a*) four 2*p* electrons.

(*b*) two 4*p* electrons.

(*c*) two electrons in a *d* subshell.

(*d*) three electrons in a 6*p* subshell.

(*e*) one electron in the 4*d* subshell.

(*f*) three electrons in the 5*d* subshell.

[Ans. (*a*) O, (*b*) Ge, (*c*) Ti, (*d*) Bi, (*e*) Y, (*f*) Ta.]

15

CHEMICAL BONDING

Atoms combine to form chemical bonds because of a decrease in potential energy with a corresponding increase in stability. Particles attract one another in a most stable relative position when they are close that is in a state of lowest potential energy. Chemical bonds form because the atoms are in a state of lower potential energy and in a more stable condition in the bonded situation then they are, when separated.

G.N. Lewis based his concept of bond formation on the observation that the noble gases are exceptionally stable and that these elements contain eight electrons in their outermost energy level. This led to the rule of eight or "octet rule", which states that atoms will bond in such a way as to attain eight electrons in their highest principal energy level. This is a simple model and works in most of the cases.

Ionic bonds are formed when the combining atoms exchange valence electrons. Covalent bonds are formed when the combining atoms share valence electrons.

Coordinate covalent, bonds are formed when both the electrons needed for the bond formation are provided by one atom, called the donor and the atom which takes this electron pair is called the acceptor. This bond is also known as the polar covalent bond.

The concept of electronegativity is very useful and helps to predict the type of bonding in the molecule. The limits established as criteria for ionic, polar covalent or covalent compounds are used as the general guidelines.

The following guidelines should be followed for writing the electron dot formula.

1. Determine the total number of valence shell electrons noting the charge on the species if there is one.

Total number of electrons=sum of valence electrons+or —charge.

2. Arrange the atoms in the order in which they are bonded in the structure.

3. Place the total number of valence shell electrons around the

atoms symmetrically in groups of two, so that all atoms have eight electrons, except hydrogen, which should have two.

4. If it is not possible to get eight electrons around the atoms (other than hydrogen) by symmetrical placement of electrons, some bonds may be double or triple bonds. Or one or more of the atoms may not obey the rule of eight.
5. The number and location of double or triple bonds usually can be determined by first placing the electrons around the atoms symmetrically in groups of two and then moving pairs of electrons to spots between atoms until each atom has eight electrons.

Pauling assumes that the ionic radius of the univalent ions is given by

$$R_1 = C_n/(Z-S), \qquad \ldots (1)$$

where C_n is a constant for isoelectronic species, Z is the nuclear charge, S is the reduction in nuclear charge sensed by the valence electrons due to screening by the inner electrons. By choosing salts composed of isoelectronic ions, one obtains the results that the univalent radii, R_1 are inversely proportional to the effective nuclear charges $(Z-S)$. The interionic distances can be determined from X-ray diffraction measurements along with the screening constants, hence R_1 can be calculated.

VSEPR method. The VSEPR method for predicting molecular shape in accord with the experiment suggests that

1. The general shape of the molecule will be determined by the symmetrical arrangement of electron pairs around atoms. The number of pairs is obtained from a correctly drawn electron-dot structure.
2. In applying the rule 1, double bonds are to be treated as if they contributed only one bonding pair to those on the central atom.
3. Lone pairs occupy more space than single-bond pairs.

Valence Bond Theory

According to this theory, bonding occurs by the exchange of electrons between the atoms forming the bond. The exchange of electrons is made possible by the overlap of valence electron orbitals of one atom with the valence electrons orbitals of another atom. Consider two atoms, each with a valence orbital with one electron in it. As these atoms are brought together, there is an attractive force which lowers the energy of the system. This attractive force is due to the overlap of orbitals permitting the exchange of electrons from one atom to another. The exchange of electrons from one atom to another places two electrons in the same orbital. Consequently, the overlap of orbitals is permitted by Pauli exclusion principle only if the electrons are of opposite spin. On the other hand, if the electrons have the same spin, there is a repulsion between the electrons causing no orbital overlap. In such a case there will be no attraction between atoms and hence no bonding.

Molecular Orbital Theory

The valence bond theory could not explain the bonding and energy level spacing in some common molecules, i.e., oxygen. Moreover, the orbitals in atoms present in the molecules would be more profoundly affected by neighbouring atomic nuclei in the same molecule than is predicted by valence bond theory. The molecular orbital theory assumes that the valence orbitals of all atoms in molecules disappear as the molecules form. A new set of molecular orbitals is thus formed. These are unique to the molecule and are controlled by all the atomic nuclei in the molecule. Each molecular orbital has a characteristic energy. A complete determination of molecular orbitals would require the solution of the Schrödinger equation for the system of two or more nuclei. This has not been done due to mathematical difficulties. This has been made mathematically tractable by postulating that the molecular orbitals are linear combination of atomic orbitals. The descriptions of the electrons can still be based on hydrogen atom wave functions, and in this way the wave function, not normalized for electron 1 of the hydrogen molecule can be written as

$$\Psi(1)=a(1)+b(1) \qquad \ldots(2)$$

and the wave function for electron 2 is

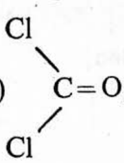
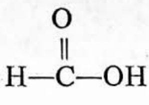
$$\Psi(2)=a(2)+b(2) \qquad \ldots(3)$$

The wave function for the pair of electrons in the molecule is then

$$\Psi=\Psi(1)\Psi(2)$$
$$\Psi=[a(1)+b(1)]\,[a(2)+b(2)]$$
$$\Psi=[a(1)\,a(2)+b(1)\,b(2)]+[a(1)\,b(2)+a(2)\,b(1)] \qquad \ldots(4)$$

The first two represent the possibility of both the electrons being on the same atom at the same time. The molecular orbital wave functions can be used to calculate the energy of the chemical bond.

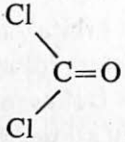
Problem 15.1. Discuss the nature of bonding in each of the following. Indicate the number of σ and π bonds, the stereochemistry, and the type of hybridization expected.

(*a*) HCN, (*b*) CO_2, (*c*) , (*d*)  $H-\overset{\overset{O}{\|}}{C}-OH$

Solution. (*a*) H—C≡N
The carbon atom is joined to the H atom by a single σ-bond and to the N atom by triple bond (i.e., one σ-bond and two π-bonds) for a total of two σ-bonds and two π-bonds. The C atom is *sp* hybridized, and the molecule is linear.

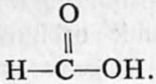
(*b*) O=C=O
The carbon atom is joined to each of the O atoms by a double bond (i.e., one σ and one π-bond) for a total of two σ-bonds and two π-bonds. The molecule is linear, and the C atom is *sp* hybridized.

(*c*)



The C atom is joined to each Cl atom by a single atom by a single σ-bond and to the O atom by a double bond (one σ-and one π-bond) for a total of three σ-bonds and one π-bond. The molecule is trigonal planar and the C atom is sp^2 hybridized.

(*d*)



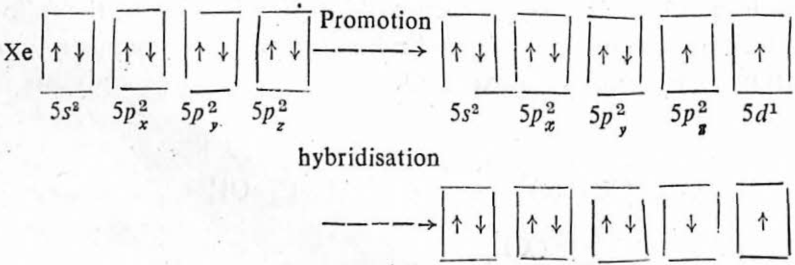
$H-\overset{\overset{O}{\|}}{C}-OH.$

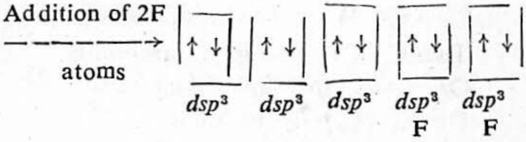
The C atom is joined to the H atom and the OH group by single σ-bonds and to the other O atom by a double bond (one σ-and one π-bond). The O atom and the H atom in the O—H group are joined by a single σ-bond. There are four σ-bonds and one π-bond in the molecule. The C atom is sp^2 hybridized (trigonal planar). The O atom in the OH group is sp^3 hybridized (angular).

Problem 15.2. The number of unshared valence electron pairs in XeF_2 is

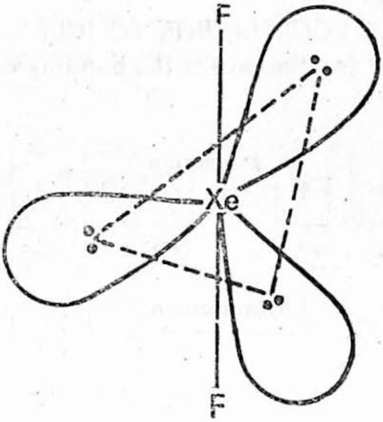
(*a*) one, (*b*) two, (*c*) three (*d*) four, (*e*) none.

Solution. To form XeF_2, one of the 5 *p* electrons must be promoted to an empty *d* orbital so that two unpaired elecrons are available for bonding:





This leaves three unshared valence electron pairs.



Problem 15.3. Which of the following molecules contain two pi bonds?

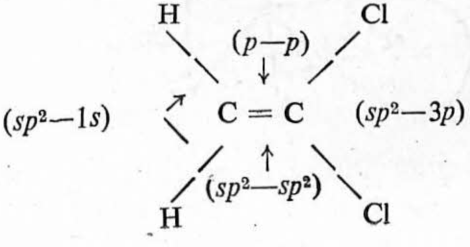
(*a*) methane, (*b*) ethane, (*c*) ethene, (*d*) ethyne, (*e*) none of these.

Solution. (*d*) H—C≡C—H One C — C *sp*—*sp* sigma bond
Two C — C *p*—*p* pi bonds
Two C — H *sp*—1s bonds.

Problem 15.4. The $CH_2{=}CCl_2$ molecule contains:

(*a*) four sigma bonds and two pi bonds
(*b*) five sigma bonds and are pi bond
(*c*) six sigma bonds
(*d*) one pi bond
(*e*) none of these.

Solution. The structure $CH_2{=}CCl_2$ can be described as



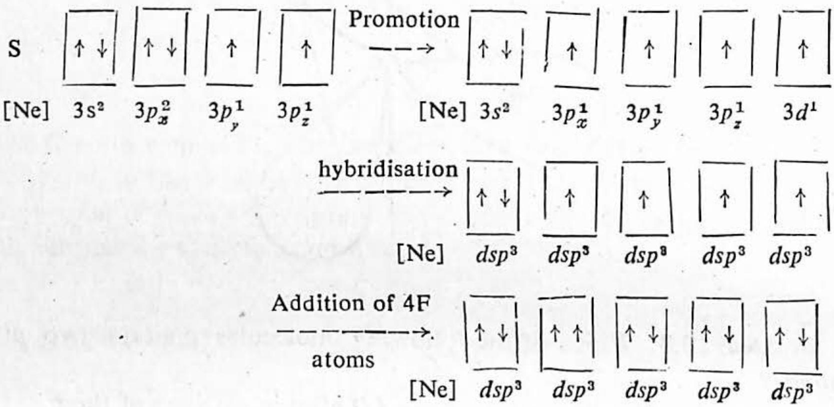
Two C—H sp^2—$1s$ sigma bonds
Two C—Cl sp^2—$3p$ sigma bonds
One C—C sp^2—sp^2 sigma bond
One C—C p—p pi bond.

Hence (*b*) is correct.

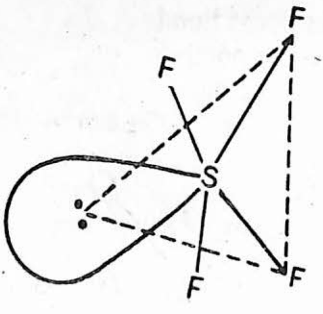
Problem 15.5. Which of the following exhibits distorted tetrahedral molecular geometry?

(*a*) BCl_3, (*b*) SF_4, (*c*) CCl_4, (*d*) BrF_5, (*e*) ICl_3.

Solution. In order to account for the bonding dsp^3 hybridisation is used.


S
↑↓ ↑↓ ↑ ↑
[Ne] $3s^2$ $3p_x^2$ $3p_y^1$ $3p_z^1$
Promotion
↑↓ ↑ ↑ ↑ ↑
[Ne] $3s^2$ $3p_x^1$ $3p_y^1$ $3p_z^1$ $3d^1$
hybridisation
↑↓ ↑ ↑ ↑ ↑
[Ne] dsp^3 dsp^3 dsp^3 dsp^3 dsp^3
Addition of 4F atoms
↑↓ ↑↑ ↑↓ ↑↓ ↑↓
[Ne] dsp^3 dsp^3 dsp^3 dsp^3 dsp^3

In SF_4 there are ten electrons—six from sulphur and one from each fluorine—or five pairs (4 bonding pairs and one lone pair). The distorted tetrahedral molecular geometry results from the lone pair of electrons. There is greater repulsion between the lone pair of electrons than between the bonding pairs of electrons.



Problem 15.6. Use VSEPR theory to predict the shapes of the following ions. All the bonds in these structures are single bonds.

(*a*) AsF_2^+, (*b*) $TiCl_2^+$, (*c*) IBr_2^-, (*d*) $SnCl_3^-$, (*e*) ClF_4^-

Assume that each halogen atom contributes one electron to the valence shell of the central atom for bond formation.

Solution. The number of valence electons of the central atom (A), plus one electron for each substituent halogen atom (X), and an adjustment for the charge of the ion (chg.) give the total number of electrons in the valence shall of the central atom. One-half of this number is the total number of electron pairs. Since each halogen is bonded by a single bond pair, the number of halogen atoms is also the number of bonding electron pairs. The number of non-bonding electron pairs is obtained by subtraction.

	Electrons	*Electron pairs*			*Shape*
	A+X+chg=total	*total*	*bdg*	*non-bdg*	
(*a*) AsF_2^+	5+2−1=6	3	2	1	angular
(*b*) $TiCl_2^+$	3+2−1=4	2	2	0	linear
(*c*) IBr_2^-	7+2+1=10	5	2	3	linear
(*d*) $SnCl_3^-$	4+3+1=8	4	3	1	trigonal pyramidal
(*e*) ClF_4^-	7+4+1=12	6	4	2	square planar.

Problem 15.7. Describe the molecular F_2 and NO in terms of the valence bond and molecular orbital theories. What advantage does one theory offer over the other in each case?

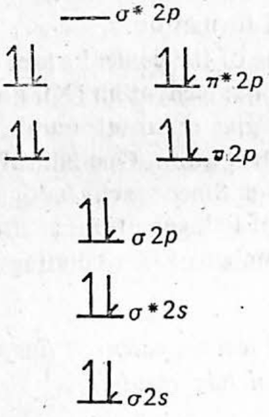
Solution. The electronic structures of F_2 and NO can be written as:

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}} - \underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:;\ .\overset{\cdot\cdot}{N} = \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$$

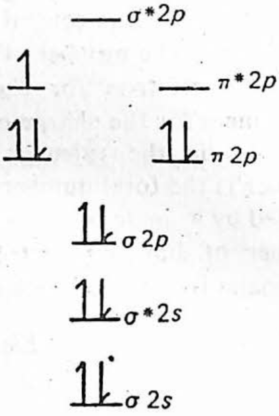
In the valence bond theory, the F-F bond is formed by overlap of a half-filled $2p$ orbital from one F with a half-filled $2p$ orbital from the other F to form a σ-bond. The remaining atomic orbitals are occupied by "lone pairs" and are not involved in bonding.

The valence bond picture of NO represents a σ-bond formed by overlap of the half-filled $2p$ orbital from O with a half-filled $2p$ orbital from N. The two remaining valence orbitals on O and one of the valence orbitals on N are occupied by lone pairs. The remaining valence orbital on N is occupied by an unpaired electron.

According to the molecular orbital theory, the atomic orbitals lose their identity when a molecule is formed and are replaced by molecular orbitals. The molecular orbital electron arrangements for F_2 and NO are as under,



M.O. Energy level diagram of
F₂ molecule



M.O. Energy level diagram of NO

In F_2 the electronic configuration is $(1s^2)$ $(1s^2)$ $(\sigma_{2s})^2$ $(\sigma_{2s}{}^*)$ $(\sigma_{2p})^2$ $(\pi_{2p})^4$ $(\pi_{2p})^4$. The predicted bond order for F_2 is 1. In NO the electronic configuration is

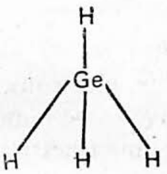
$$(\sigma_{1s}{}^2)\ (\sigma_{1s}{}^2)\ (\sigma_{2s}{}^2)\ (\sigma_{2s}{}^*)^2\ (\sigma_{2p})^2\ (\pi_{2p})^4\ (\pi_{2p})^1.$$

The bond order predicted for NO is $2\frac{1}{2}$.

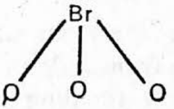
The valence bond theory is more easily represented pictorially than the molecular orbital theory which is better at predicting bond orders and bond strengths. Both the theories predict correctly the paramagnetic nature of NO.

Problem 15.8. Predict the shape and expected hybridization of (*a*) GeH_4, (*b*) BrO_3^-, (*c*) SF_6, (*d*) PBr_5, (e) HOCl.

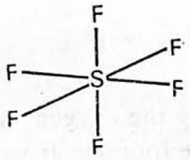
Solution.



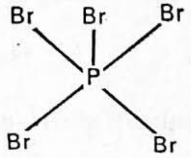
Tetrahedral *sp*³



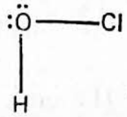
Pyramidal *sp*³



Octahedral *d*²*sp*³



Trigonal pyramid *dsp*³



Angular *sp*³

Problem 15.9. Show that oxygen is a paramagnetic substance.

Solution. In oxygen (O_2) we have to take care of 16 electrons, eight for each oxygen atom. The molecular orbital in O_2 are,

$$\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p^2\ \pi_y 2p^2=\pi_z 2p^2\ \overset{*}{\pi}_y 2p^1=\overset{*}{\pi}_z 2p^1$$

We see that there are ten bonding electrons and six antibonding electrons, thus leaving a net of four bonding electrons or two bonding electron-pairs. A bond consisting of two pairs of bonding electrons is often called a double bond. Note that there are two unpaired electrons in the O_2 electrons, one in the $\pi_y{}^*2p$ orbital and one in $\pi_z{}^*2p$ orbital. Here the molecular orbital model fits well the experimental fact that oxygen is paramagnetic.

Problem 15.10. Which is likely to have a more stable electron distribution O_2 or $O_2{}^+$ and N_2 or $N_2{}^+$?

Solution. O_2 has the electron configuration;

$$\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p^2\ \pi_y 2p^2=\pi_z 2p^2\ \pi_y{}^*2p^1=\pi_z{}^*2p^1$$

It has 10 bonding electrons; 6 antibonding electrons.

To make $O_2{}^+$, the least stable electron, $\pi_y{}^*2p$ or $\pi_z{}^*2p$ is removed. There are 10 bonding and 5 antibonding electrons, so $O_2{}^+$ should be somewhat more stable in terms of electron distribution. N_2 has the electron configuration

$$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi_y 2p^2 = \pi_z 2p^2$$

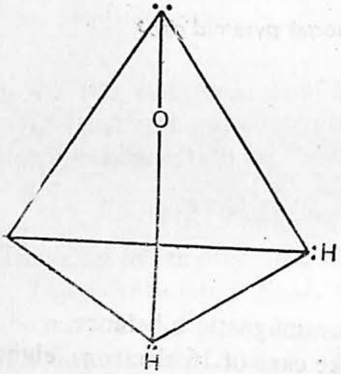
It has 10 bonding electrons and 4 antibonding electrons. To make N_2^+, an electron from $\pi_y 2p$ or $\pi_z 2p$ would have to be removed. There would then be 9 bonding and 4 antibonding electrons, thus N_2^+ should be less stable than N_2.

Problem 15.11. Determine the shape of a water molecule.

Solution. The dot formula for H_2O is

$$\mathrm{H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : H}$$

There are four pairs of electrons surrounding the oxygen atom, consequently the four electron pairs will occupy the corners of a tetrahedron. Here two of the electron pairs are bond pairs and two are lone pairs. Since all the four corners of a tetrahedron are equivalent, it is completely arbitrary which two corners are occupied by H atoms. Water molecule has two bond pairs and two lone pairs. The repulsion between the lone pairs is more than between bond pairs, this makes water molecule bent or angular.



Problem 15.12. Calculate the lattice energy of sodium chloride. The smallest anion-cation distance r_o is 2.81 Å. The Madelung constant for NaCl is 1.747 and $n=0.80$ ($e^2=23.1=10^{-20}$ erg cm).

Solution. If only coulombic term and Born repulsion terms are considered and ignoring weak van der Waals interactions, the lattice energy U_o is given by

$$U_o = \frac{NAZ^2e^2}{r_o}\left(1-\frac{1}{n}\right)$$

where N is Avogadro's number, A is Madelung constant terms of the shortest anion, cation distance r_o, Z is the largest common factor in the charges on the ions, n is Born exponent, e is electronic charge

$$U_o = \frac{6.0\times10^{23}\times1.747\times2.31\times10^{-20}\text{ erg cm}\times(7/8)}{2.81\times10^{-8}\text{ cm}}$$

$$U_o = 8.62\times10^{13}\text{ erg mole}^{-1}\times(7/8)$$

$$U_o = 206.2\text{ k. cal mole}^{-1}\times(7/8)$$

$$U_o = 180.4\text{ k. cal mole}^{-1}.$$

Problem 15.13. Assuming the following values for λ. calculate the per cent ionic character of the bonds in H_2, HCl and CsF.

H_2 $\lambda=0.25$
HCl $\lambda=0.45$
CsF $\lambda=3.17$

Solution. The form of wave function is given by

$$\phi_{VB}=\phi_{cov}+\lambda\phi_{ion}$$

$$\text{Per cent ionic character}=\frac{100\lambda^2}{1+\lambda^2}$$

$$H_2 \text{ per cent}=\frac{100\times0.25\times0.25}{1+0.25\times0.25}$$

$$H_2 \text{ per cent}=3.846$$

$$\text{HCl per cent}=\frac{100\times0.45\times0.45}{1+0.45\times0.45}$$

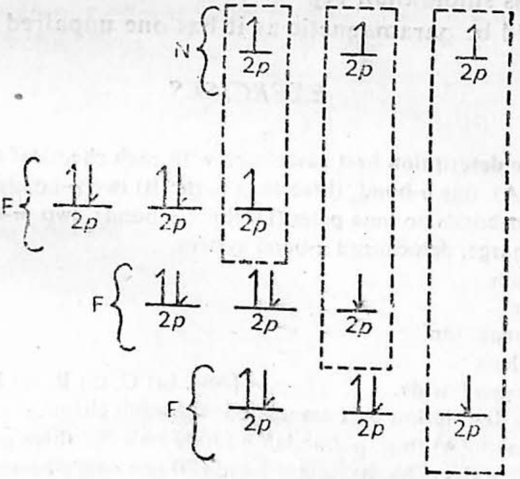
$$\text{HCl per cent}=16.84$$

$$\text{CsF per cent}=\frac{100\times3.17\times3.17}{1+3.17\times3.17}$$

$$\text{CsF per cent}=90.95.$$

Problem 15.14. Give the valence bond representation for bonding in the molecule NF_3. Which orbitals overlap to form the bonds?

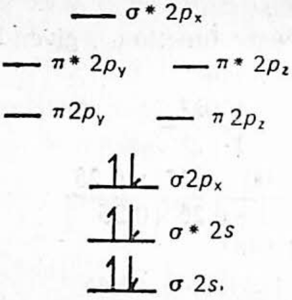
Solution.



Since the 2*s* electrons are not involved in bonding, they do not have to be included in the representation. The 2*p* orbitals of nitrogen and 2*p*′ orbitals of fluorine overlap.

Problem 15.15. Write down the MO designation for N_2^-. What is its bond order and stability compared to N_2? Would it be paramagnetic?

Solution. The MO picture of N_2^- would be



M.O. picture of N_2^-

N_2^- requires 11 valence electrons:

5 valence electrons for each atom +1 extra electron for charge. The extra electron may occupy either π^*2p_y or π^*2p_z because they are of equal energy.

$$\text{Bond order} = \tfrac{1}{2}(8-3)$$
$$= 2.5$$

N_2 Bond order $= 3$

∴ N_2^- is less stable than N_2.

Yes it would be paramagnetic as it has one unpaired electron.

EXERCISES

15.1. Select the description best associated with each chemical species.
Terms: (A) one σ-bond, three lone pairs (B) two σ-bonds, two lone pairs (C) four σ-bonds no lone pairs (D) three σ-bonds, two π-bonds (E) delocalized charge, delocalized π-bond system.
(*a*) methane
(*b*) water
(*c*) carbonate ion
(*d*) acetylene
(*e*) hydrogen floride. [Ans. (*a*) C, (*b*) B, (*c*) E, (*d*) D, (*e*) A.]

15.2. Select the description best associated with each chemical species.
Descriptions: (A) four σ-bonds, no lone pair (B) three σ-bonds one lone pair (C) five sigma bonds, one π-bond (D) one single bond, one triple bond (E) delocalized charge, delocalized π-bond system.
(*a*) ammonia
(*b*) ammonium ion
(*c*) ethylene

(*d*) hydrogen cyanide
(*e*) nitrate ion. [Ans. (*a*) B, (*b*) A, (*c*) C, (*d*) D, (*e*) E.]

15.3. Indicate the angle between:
(*a*) sp^3 hybrid orbitals
(*b*) sp^2 hybrid orbitals
(*c*) *sp* hybrid orbitals
(*d*) *p* orbitals
(*c*) sigma bonds in SF_6.

[Ans. (*a*) 109.5°, (*b*) 120°, (*c*) 180°, (*d*) 90°, (*e*) 90°.]

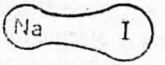
15.4. Indicate the molecular geometries expected for
(*a*) carbon dioxide,
(*b*) carbon tetrafluoride,
(*c*) aluminium bromide,
(*d*) nitrogen triiodide.

[Ans. (*a*) linear, (*b*) tetrahedral, (*c*) trigonal planar, (*d*) pyramidal.]

5.5. Select the term best associated with each definition, description or specific example.

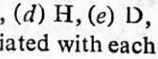
Terms: (A) covalent radius (B) diffusion (C) elastic collision (D) hydrogen bonds (E) hydrophilic (F) ionic radius (G) mean free path (H) metallic bond (I) solvent (J) temperature.

(*a*) characterized by conservation of momentum,
(*b*) average distance between successive collisions in a collection of moving particles,
(*c*) a function of the average kinetic energy of the particles in a system,
(*d*) principal forces among neighbouring atoms in a crystal,
(*e*) principal forces among neighbouring water molecules in ice,
(*f*) the substance acting to dissolve another substance,
(*g*) movement of HCl molecules through the air,
(*h*) a molecule or atomic grouping strongly attracted to water molecules,
(*i*) distance indicated



I_2 molecule

(*j*) distance indicated



NaI molecule

[Ans. (*a*) C, (*b*) G, (*c*) J, (*d*) H, (*e*) D, (*f*) I, (*g*) B, (*h*) E, (*i*) A, (*j*) F.]

15.6. Select the best terms associated with each definition, description of specific example.

Terms: (A) Covalent radius (B) Dipole-dipole forces (C) Hydrogen bonds (D) Hydrophobic (E) Inelastic collisions (F) London, dispersion forces (G) Metallic radius, (H) Solute (I) Translation (J) van der Waals radius.

(*a*) movement of atoms in helium gas to new relative positions,
(*b*) characterized by a net change in momentum,
(*c*) principal forces among neighbouring molecules in liquid hydrogen,
(*d*) principal forces among neighbouring molecules in liquid ammonia,
(*e*) principal forces among neighbouring molecules in liquid hydrogen bromide,
(*f*) the substance being dissolved by another,
(*g*) molecules or atomic groupings not attracted by water,
(*h*) one-half the internuclear distance in the hydrogen molecule,
(*i*) one-half the internuclear distance between adjacent atoms in liquid neon,
(*j*) one-half the internuclear distance between adjacent atoms in crystalline potassium.

[**Ans.** (*a*) I, (*b*) E, (*c*) F, (*d*) C, (*e*) B, (*f*) H, (*g*) D, (*h*) A, (*i*) J, (*j*) G.]

15.7. Using VSEPR method predict the shape of each of the following
(*a*) NH_4^+, (*b*) $BeCl_2$, (*c*) H_2Se, (*d*) PCl_3, (*e*) NH_2^-, (*f*) AsF_5, (*g*) IF_2^-.

[**Ans.** (*a*) tetrahedral, (*b*) linear, (*c*) angular, (*d*) pyramidal, (*e*) angular, (*f*) trigonal bipyramid, (*g*) linear.]

15.8. Use VSEPR method to predict the shape of each of the following:
(*a*) SF_5^-, (*b*) XeF_3^-, (*c*) ClF_4^-, (*d*) XeF_4, (*e*) IF_3, (*f*) ICl_2^+.

[**Ans.** (*a*) square pyramidal, (*b*) T-shaped, (*c*) square planar, (*d*) square planar, (*e*) T-shaped, (*f*) angular.]

15.9. Which of the following does not apply to the phrase "antibonding orbital"?
(*i*) involves an energy higher than that of the atomic orbital.
(*ii*) involves an energy not conducive to increased stability.
(*iii*) a designation related to the molecular orbital model or bonds.
(*iv*) an expression used when an electron is removed from an atom.

[**Ans.** (*iv*).]

15.10. Each of the following has something to do with the bonding capacity of an atom except
(*i*) the number of unpaired electrons,
(*ii*) the number of half occupied orbitals,
(*iii*) the spin on the outer electron,
(*iv*) the number of valence electrons. [**Ans.** (*iii*).]

15.11. Which best explains the stability of all chemical bonds?
(*i*) increased attractions between electrons and nuclei,
(*ii*) eight electrons in the valence orbits of all atoms,
(*iii*) formation of positive and negative ions,
(*iv*) empty valence orbitals in the bonding atoms. [**Ans.** (*i*).]

15.12. Which is not a condition for a molecule to be a dipole?
(*i*) there must be bonds with ionic character,
(*ii*) there must be at least one double bond in the molecule,
(*iii*) the molecule must possess a favourable shape,
(*iv*) there must be at least two different elements in the molecule.

[**Ans.** (*ii*).]

15.13. Which most favours a high lattice energy in ionic compounds?

(*i*)	small ion,	high charge
(*ii*)	small ion,	low charge

(*iii*) large ion, high charge
(*iv*) large ion, low charge. [Ans. (*i*).]

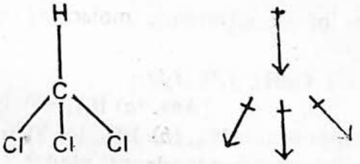
15.14. The process by which the gaseous hydrogen chloride dissolves in water might be described best as
(*i*) proton transfer, (*ii*) hydrogen bonding, (*iii*) ionic dissociation, (*iv*) van der Waals force. [Ans. (*i*)]

15.15. Predict in which of the two solvents H_2O or $CHCl_3$, the following solutes would be most soluble.
(*a*) CH_4, (*b*) CO_2, (*c*) $Ca(OH)_2$, (*d*) YCl_3, (*e*) I_2, (*f*) Na_2CO_3, (*g*) $FeCl_3$, (*h*) C_6H_6.
[Ans. (*a*) $CHCl_3$, (*b*) $CHCl_3$, (*c*) H_2O, (*d*) H_2O, (*e*) $CHCl_3$, (*f*) H_2O, (*g*) H_2O, (*h*) $CHCl_3$.]

15.16. Predict whether the solvation energy will be high or low when the following substances are mixed with H_2O:
(*a*) SO_2(g), (*b*) N_2(g), (*c*) KF(s), (*d*) YCl_3(s), (*e*) SiH_4(g), (*f*) Cl_2(g), (*g*) Ar(g), (*h*) NaOH(s), (*i*) HCl(g).
[Ans. (*a*) high, (*b*) low, (*c*) high, (*d*) high, (*e*) low, (*f*) low, (*g*) low, (*h*) high, (*i*) high.]

15.17. Predict whether or not the following bonds are polar and, if so which atom is the more positive? (*a*) $N\equiv N$, (*b*) $B-N$, (*c*) $S-Cl$, (*d*) $P=O$.
[Ans. (*a*) non-polar; (*b*) yes, B; (*c*) yes, S; (*d*) yes, P.]

15.18. Predict which of the following molecules would be polar and explain each in terms of polar and nonpolar covalent bonds and the geometry of these bonds? If the molecule is polar, give the direction of the dipole moment from the positive to the negative side.
(*a*) Hydrogen flouride, HF
(*b*) Chloroform, $CHCl_3$
(*c*) Acetylene C_2H_2
(*d*) Bromine, Br_2.
[Ans. (*a*) Yes, HF bond is polar, centre of positive charge is located to the left of centre of negative charge; (*b*) Yes.

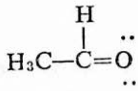


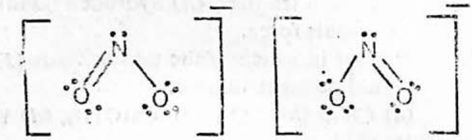
All bonds are polar. The centre of positive charge is above the centre of the negative charge.]

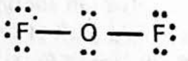
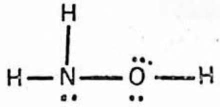
(*c*) $\overset{\leftarrow+}{H-C}\equiv\overset{+\rightarrow}{C-H}$. The bonds are slightly polar but the centre of the positive charge and the centre of the negative charge are both at the centre of the molecule.

(*d*) no, a non-polar bond.

15.1^0. Draw the octet structural formulas for each of the following
(*i*) CH_2Cl, (*ii*) C_2H_4O, (*iii*) NO_2^-, (*iv*) OF_2, (*v*) NH_3O.

[**Ans.** (*i*) H—C≡C—Cl, (*ii*) 
$H_3C{-}\overset{\displaystyle H}{\overset{|}{C}}{=}\ddot{\underset{..}{O}}$

(*iii*) 

(*iv*)  

15.20. The chlorine-oxygen bond distance in ClO_4^- is 1.44 Å. What do you conclude about the valence bond structures for this ion?

[**Ans.** There must be a considerable double bond character in the bonds.]

15.21. What is the length of a polymer molecule containing 1001 carbon atoms singly bonded if a line of the molecule could be stretched to its maximum length consistent with maintenance of the normal tetrahedral angle within any C—C—C group? [**Ans.** 1.26×10^3 Å.]

15.22. A plant virus was examined by the electron microscope and was found to consist of uniform cylindrical particles 150Å in diametre and 3000Å long. The virus has a specific volume of 0.73 c.c./g. If the virus particle is considered to be one molecule, what is its molecular weight?

[**Ans.** 4.4×10^7.]

15.23. Draw electron dot formulas for (*a*) HCl, (*b*) CO, (*c*) NO^+, (*d*) CN^-, (*e*) N_2.

[**Ans.** (*a*) $\mathrm{H : \overset{..}{\underset{..}{Cl}} :}$ (*b*) $\mathrm{: C : : : O :}$ (*c*) $\mathrm{: N : : : O^+ :}$ (*d*) $\mathrm{: C : : : N^-}$

(*e*) $\mathrm{: N : : : N :}$]

15.24. Give the formula of a polyatomic molecule that will have the same shape as

(*a*) IF_3, (*b*) PCl_3, (*c*) GeH_4, (*d*) H_2O.

[**Ans.** (*a*) ICl_3, (*b*) NF_3, (*c*) CH_4, (*d*) H_2S.]

15.25. Determine the shapes of (*a*) OF_2, (*b*) BF_3, (*c*) PCl_5.

[**Ans.** (*a*) bent or angular, (*b*) trigonal planar, (*c*) trigonal bipyramid.]

15.26. Predict whether the following molecules are ionic, covalent or polar covalent.

(*a*) H_2O, (b) KCl, (*c*) BaI_2, (*d*) I_2.

(**Hint:** Calculate the electronegativity difference in each case.)

[**Ans.** (*a*) polar, (*b*) ionic, (*c*) polar covalent, (*d*) covalent.]

15.27. Which of the following molecules should be more ionic than the others?

(*a*) HF, HCl, HBr; (*b*) $BeCl_2$, $MgCl_2$, $BaCl_2$.

[**Hint** : (*a*) calculate the electronegativity difference. This is highest in the case of HF (1.9) as compared to HCl (0.9) or HBr (0.7).]

(*b*) $BaCl_2$ is most ionic because electronegativity difference i.e. (2.10) is greater than $MgCl_2$ (1.8) and $BaCl_2$ (1.5).]

15.28. $BaCl_2$ and $TeCl_2$ are both covalent molecules. Yet $BeCl_2$ is linear while $TeCl_2$ is "V" shaped. Explain.

[**Ans.** $BeCl_2$ is Cl : Be : Cl whereas $TeCl_2$ has two lone pairs, therefore $TeCl_2$ is "V" shaped just like H_2O molecule.]

15.29. SF_6 is a perfect octahedron but XeF_6 is a distorted octahedron. Explain.

[**Ans.** There are six electron pairs, all bond pairs in SF_6 hence a perfect octahedron, whereas in XeF_6 there are seven electron pairs, one of them being a lone pair that must "stick out" somewhere, thus distorting a perfect octahedron.]

15.30. Based upon electron configurations and octet rule, explain the following:

(*a*) VF_5 exists but VF_6 does not.

(*b*) $TiCl_4$ is much more stable than $TiCl_3$.

(*c*) Carbon forms two types of carbides, C^{4-} and C_2^{2-}.

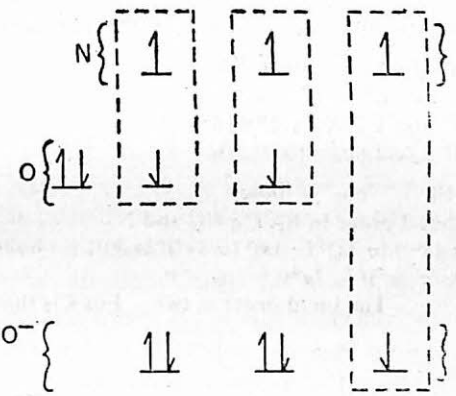
[**Ans.** (*a*) V has an "Ar" structure in VF_5 where as VF_6 would involve breaking into a stable octet and hence unstable.

(*b*) Ti obeys the octet rule in $TiCl_4$ but not in $TiCl_3$.

(*c*) C^{4-} and (: C : : : C : $)^{2-}$ both obey the octet rule.]

15.31. Give the valence bond representation for bonding in the NO_2 ion. Which orbitals overlap to form the bonds?

[**Ans.**



Orbitals of NO_2^-

The $2p^1$ orbitals of oxygen overlap the $2p'$ orbitals of the nitrogen. There is a double bond between nitrogen and one oxygen.]

15.32. Of the three types of hybrid orbitals, *sp*, sp^2, and sp^3 which has the maximum *s* character? [**Ans.** *sp* contains 50 per cent *s* character.]

15.33. What type of hybridization would account for the following?

(*a*) SO_3 molecule is planar with O−S—O bond angles of 120°.

(*b*) H−As—H bond angle in AsH_3 is 109°.

(*c*) O−N O bond angle in NO_3^- is 120°.

(*d*) Cl—Sb−Cl bond angle in $SbCl_3$ is 190°.

[**Ans.** (*a*) sp^2, (*b*) sp^3, (*c*) sp^2, (*d*) sp^3.]

15.34. Determine the values of the normalized wave function $S_A + S_B$ for the hydrogen molecular ion at the position of one of the protons and at the centre of the molecule. Where does the wave function have a larger value?

[Ans. On a proton $\psi=0.359601$ at mid point $\psi=0.233041$.]

15.35. Which method gives the best result for the bond energy of the hydrogen molecule, the valence bond (VB) method or the molecular orbital method? Can you explain this result?

[Ans. The valence bond method gives the best result because it includes some correlation and because the MO method over-represents ionic structures.]

15.36. Predict the molecular shape for the following:

(*a*) ICl_4, (*b*) $TeCl_4$, (*c*) IF_5, (*d*) PCl_5.

[Ans. (*a*) square planar, (*b*) irregular tetrahedron, (*c*) square pyramid, (*d*) trigonal bipyramid.]

15.37. The electric dipole moment of the NH_3 molecule *is* 1.47D and the dipole moment of the NF_3 molecule is 0.21D. Explain the relative magnitudes of these numbers and in particular, why the NF_3 moment is so small in spite of the large difference in electronegativity contants between N and F.

[Ans. The NH_3 dipole moment is due to the lone pair of electrons on the nitrogen, the NH bond moments have the opposite directions but they are small. The NF bond moments are larger than NH bond moments and they cancel the lone pair moments more or less.]

15.38. Assuming ψ_{cov} (HCl) is completely non-polar and all the polarity of HCl molecule derives from ψ_{ionic}, calculate the per cent ionic character for HCl wave function using the following data:

$$\mu=1.03\times10^{-18}\text{ esu}=1.03\text{ Debye}$$
$$r_0=1.27\,\text{Å}=1.27\times10^{-8}\text{ cm}$$
$$e=4.802\times10^{-10}\text{ esu}$$

[Hint: $\psi_{\text{HCl}}=\psi_{\text{cov}}+\lambda\psi_{\text{ionic}}$.] [Ans. 17 per cent.]

15.39. Predict the bond order in B_2, C_2, Cl_2 and N_2.

[Ans. B_2, $(\sigma\, 1s^a)^2\,(\sigma\, 1s)^2\,(\sigma\, 1s)^2\,(\sigma\, 2s^a)^2\,(\sigma_z b)^2$; bond order is one;
C_2 kk $(\sigma\, 2s^b)^2\,(\sigma\, 2s^a)^2\,(\pi 2p_{x,y}{}^b)^4$.
The bond order is two. For Cl_2 the bond order is one.]

16

PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

INRTODUCTION

Molecular spectroscopy may be defined as the study of interaction of electromagnetic waves and matter. A molecule in space can have different forms of energy, e.g., rotational energy by virtue of bodily rotation about its centre of gravity, vibrational energy due to the periodic displacement of its atoms from their equilibrium positions; electronic energy resulting from continuous motion of electrons associated with each atom or bond. The energy of a molecule is the sum (total) of these energies. The spacing of the translational energy levels is extremely small and the neutral molecules cannot interact with radiation and thereby change from one translational level to another. The spectroscopic studies can be classified as rotational, vibrational or electronic spectroscopy. If a sample is placed in an electric or magnetic field, it is possible to study transitions between energy levels resulting from the interaction of the molecules or the atoms of the molecules, with the applied field. Each kind of energy level in a molecule is characterized by a quantum number, designated by the symbols as follows: n is used to denote electronic level, as to denote vibrational level and J to denote rotational levels. Electronic transitions between levels with any values of n are possible, but it turns out that rotational and vibrational transitions can occur only between energy states which have rotational or vibrational quantum numbers differing by l, i.e.,

$$\triangle v = \pm 1. \qquad \triangle J = \pm 1$$

Such limitations on quantum number changes are called selection rules.

Pure rotational spectra are observed in the far infra-red and microwave region of the electromagnetic spectrum, provided that the molecule has a permanent dipole. Analysis of the rotational spectra helps us to determine the bond lengths of heteronuclear diatomic molecules.

For a diatomic molecule AB, the energies of the rotational levels are given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \qquad \ldots (1)$$

where J is the rotational quantum number and I is the moment of inertia. The frequency of the absorbed light, when a molecule is raised in rotational energy is given by

$$\nu = \frac{h}{4\pi^2 I} \cdot J \qquad \ldots (2)$$

On the other hand, all the vibrations of a molecule can be described as one or a combination of certain number of fundamental modes of vibration. A linear molecule has $3n$-5 fundamental modes of vibration and a non-linear molecule has $3n$-6 such modes. However, of several possible fundamental vibrations of a given molecule only those vibrations accompanied by a change in dipole moment will be infra-red active. The numbers of fundamental molecular vibrations which are infra-red active and/or Raman active can be predicted for any molecular geometry. The proposed molecular geometry is confirmed by the agreement of its observed spectrum with the predicted spectrum. The results of such predictions for several types of molecules are given in Table 16.1.

TABLE 16.1: Theoretical infra-red and Raman activities of representative types of molecules AB_x

Geometry	*Formula type*	*Total number of vibrations*	*Infra-red active*	*Raman active*	*Inactive*
Linear	BAB	4	$\nu_2 \nu_3^*$	ν_1	
Linear	ABB	4	$\nu_1\ \nu_2\ \nu_3^*$	$\nu_1\ \nu_2\ \nu_3^*$	
Angular	AB_2	3	$\nu_1\ \nu_2\ \nu_3$	$\nu_1\ \nu_2\ \nu_3$	
Planar	AB_3	6	$\nu_2\ \nu_3^*\ \nu_4^*$	$\nu_1\ \nu_4^*$	
Pyramidal	AB_3	6	$\nu_1\ \nu_2\ \nu_3^*\ \nu_4^*$	$\nu_1\ \nu_2\ \nu_3^*\ \nu_4$	
Square planar	AB_4	9	$\nu_2\ \nu_5^*\ \nu_6^*$	$\nu_1\ \nu_3\ \nu_4^*$	
Tetrahedral	AB_4	9	$\nu_3{\dagger}\ \nu_4{\dagger}$	$\nu_1\ \nu_2^*\ \nu_3{\dagger}\ \nu_3{\dagger}$	
Octahedral	AB_6	15	$\nu_3{\dagger}\ \nu_4{\dagger}$	$\nu_1\ \nu_2^*\ \nu_5{\dagger}$	

*denotes doubly degenerate vibrations.

†denotes triply degenerate vibrations.

NMR Spectra

In the analysis of high resolution NMR spectrum the following points must be kept in mind.

1. Protons on atoms adjacent to highly electronegative atoms are highly deshielded, and their chemical shifts are downfield. The chemical shifts of protons directly bonded to highly electro-negative atoms are even more deshielded and are further downfield.
2. Protons on the same atom, and some other special groups such as the protons of the benzene molecule, are equivalent molecules of a set. The signal of a given proton in a set is not split by spin-spin interactions with other members of the set.
3. The number of lines into which the signal of a given set of protons is split by a set of protons on the adjacent atoms is $n+1$, where n is the number of protons on the adjacent atom. The second fact can be used to determine which sets of protons are on adjacent atoms.
4. The magnitudes of the spin-spin splittings for protons on adjacent carbon atoms range from 2 to 10 ppm, i.e., the symmetrical patterns of lines will be as much as 10 ppm wide. Protons on the other adjacent atoms exert a much weaker effect.

Beer-Lambert Law

It may be stated as

$$I/I_o=e^{-kbc}, \qquad \ldots (3)$$

where b is the path length, c is the concentration. The absorbance A is defined as,

$$A = \varepsilon bc \qquad \ldots (4)$$

where ϵ is the molar extinction coefficient. Another form of A is,

$$A = 2 - \log T \qquad \ldots (5)$$

where T is the transmittance.

Molar Refraction

The refractive index n depends upon the wavelength of the light and upon the fields in the light path. Experimentally n increases with decreasing wavelength of light and with increasing pressure and decreasing temperature. The refractive index n is a property of the material and is extremely useful in chemical analysis and process control. Another useful quantity is called molar refraction and is defined as

$$R_M=\frac{n^2-1}{n^2+1}\cdot\frac{M}{\rho} \qquad \ldots (6)$$

where R_M=molar refraction, M = molecular weight, ρ=density. The molar refraction depends upon the number and the kinds of atoms and bonds present. Experimental values of R can be used to distinguish between structural isomers (see Table 16.2.)

TABLE 16.2. Moler refraction contributions (for sodium D-light.)

Carbon	2.418	Oxygen (in CO group O =)	2.211
Hydrogen	1 100	Oxygen (in OH group O—)	1.525
Chlorine	5.967	Oxygen (in ethers, O—)	1.643
Bromine	8.865	Three membered ring	0.71
Iodine	13.900	Four membered ring	0.48
Double bond	1.733		
Triple bond	2 398		

Molar polarisation

The dipole moment of a molecule, *AB* is defined as the distance between the centres of positive and negative charges modified by the size of one of them, i.e.,

$$\mu=qr \qquad \ldots (7)$$

where q is the charge and r is the distance in centimetre. Generally the charge is measured in esu. Dipole moment is measured in Debye where one Debye is given by

$$1 \text{ Debye}=1\times 10^{-18} \text{ esu-cm.}$$

The values of dipole moments for most inorganic componds range from 0 to about 12. To obtain the molecular dipole moment from the observed dielectric constant a quantity called molar polarisation, *P* is used. This is defined as

$$P=\frac{D-1}{D+2}\cdot\frac{M}{\rho} \qquad \ldots (8)$$

where *P* is molar polarisation, *M* is molecular weight, ρ is density and *D* is dielectric constant. Also,

$$P=4/3\pi N\alpha+4/3\pi N\left(\frac{\mu^2}{3\alpha T}\right) \qquad \ldots (9)$$

where α is the polarizability and the term $\frac{4}{3}\pi N\alpha$ may be approximated by M_r, and μ is the dipole moment.

Parachor

It is both an additive and constitutive property and hence the parachor values can decide the correct structure out of the different structures known for the given substance. It is defined as:

$$\left(\frac{M}{D-d}\right)\gamma^{\frac{1}{4}}=MC^{1/4}=[P] \qquad \ldots (10)$$

The constant [*P*] is called the parachor. *D* is the density of the liquid and d is the density of the vapour. Since $D>>>d$, d can be neglected Hence equation (10) can be written as

$$\left(\frac{M}{D}\right)\gamma^{1/4}=[P] \qquad \ldots (11)$$

where γ is the surface tension of the liquid. M/D is called the molar volume. The parachor values of some atoms and structural fragments are given in Table 16.2.

TABLE 16.2. Parachor values

Carbon	4.8	double bond	23.2
Hydrogen	17.1	triple bond	46.6
Oxygen	20.0	3 ring	16.7
Nitrogen	12.5	4 ring	11.6
Chlorine	53.8	5 ring	8.5
Bromine	68.0	6 ring	6.1
		single bond	0.0

Optical Rotation

It refers to the ability of certain compounds to rotate the plane of polarized light. Such compounds are said to be optically active and contain at least one asymmetry centre and no plane of symmetry. The specific rotation $[\alpha]^t_\lambda$ is given by the relation,

$$[\alpha]_\lambda^t=\frac{\theta\times 100}{l\times c}$$

where, θ is the observed rotation in degrees

l is the pathlength in decimetres

c is the concentration of the solution (g/100 ml)

t is the temperature of the solution

λ is the wavelength of the polarized light generally it is taken as D-line of sodium, 5893 Å

Optical rotation is measured in an instrument called polarimeter.

Problem 16.1. Convert 2000 Å to (*i*) cm, (*ii*) cm^{-1}, (*iii*) eV, (*iv*) erg, (*v*) cal, and (*vi*) Hz.

Solution.

(*i*) $2000\text{Å}=2.00\times 10^3$ Å

$1\ \text{Å}=10^{-8}$ cm

$2000\ \text{Å}=2.00\times 10^3\times 10^{-8}\ \text{cm}=2.00\times 10^{-5}$ cm.

(*ii*) $\frac{1}{2.00}\times 10^5=5.00\times 10^4\ \text{cm}^{-1}$.

(*iii*) $5.00\times 10^4\ \text{cm}^{-1}$

$1\ \text{eV}=8068.3\ \text{cm}^{-1}$

$$\frac{5.00\times 10^4}{8068.3}=6.200 \text{ eV}$$

(*iv*) $$E=\frac{hc}{\lambda}=\frac{6.626\times 10^{-27}\text{ erg-sec.}\times 3.00\times 10^{10}\text{ cm sec}^{-1}}{2.00\times 10^{-5}\text{ cm}}$$

$$=9.940\times 10^{-12}\text{ erg/molecule.}$$

(*v*) $1 \text{ eV}=23.06 \text{ cal. mole}^{-1}$

$6.200\times 23.06 \text{ cal. mole}^{-1}$

$=1.430\times 10^5 \text{ cal. mole}^{-1}$.

(*vi*) $\lambda\times\nu=c$

$2.00\times 10^{-5}\text{ cm}\times\nu=3.00\times 10^{10}\text{ cm/sec}$

$$\nu=\frac{3.00\times 10^{10}\text{ cm/sec.}}{2.00\times 10^{-5}\text{ cm}}$$

$$=1.5\times 10^{15}\text{ Hz.}$$

Problem 16.2. Hydrogen bromide gives a series of lines in the far infra-red having a separation of 16.94 cm^{-1}. Calculate the moment of inertia of the molecule and the internuclear distance. (H=1.008, Br=79.92).

Solution. For the transition from $J=1$ to $J=0$,

$$\nu=\frac{2h}{8\pi^2 I}\cdot J$$

$$16.94\times 3.00\times 10^8=\frac{2\times 6.624\times 10^{-34}}{8(3.142)^2\, I}$$

$$\therefore \qquad I=\frac{2\times 6.624\times 10^{-34}}{8(3.142)^2\times 1694\times 3.00\times 10^8}\text{ kg m}^2$$

$$I=3.302\times 10^{-47}\text{ kg m}^2$$

$$I=\mu r^2$$

where μ is the reduced mass and r is the internuclear distance

$$I=\left(\frac{m_1m_2}{m_1+m_2}\right)r^2$$

$$3.303\times 10^{-47}=\left(\frac{m_1m_2}{m_1+m_2}\right)r^2$$

$$3.303\times 10^{-47}=\frac{1.008\times 79.92\times 10^{-3}}{(1.008+79.92)}\times\frac{r^2}{6.02\times 10^{23}}$$

$$r=\sqrt{\frac{3.302\times 10^{-47}\times 6.02\times 10^{23}\times 80.93}{1.008\times 79.92\times 10^{-3}}}\,m$$

$$r=1.413\times 10^{-10}\,m$$

Problem 16.3. The infra-red spectrum of HCl shows a maximum at 2886 cm^{-1} and the corresponding band in DCl occurs at 2091 cm^{-1} An absorption at 3312 cm^{-1} in HCN is found to shift to 2629 cm^{-1} on deuteration. Assume that these bands arise from the $X-H$ and $X-D$ modes of vibration respectively (X=Cl or CN), calculate the expected shift, and comment on any difference between theory and experiment.

Solution. The stretching frequency of a diatomic molecule is given by

$$\bar{\nu}=\frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where c is the velocity of light, k is the force constant and μ is the reduced mass

$$\tilde{\nu}(\mathrm{HCl})/\tilde{\nu}(\mathrm{DCl})=\sqrt{\frac{\mu(\mathrm{DCl})}{\mu(\mathrm{HCl})}}$$

$$\tilde{\nu}(\mathrm{HCl})/\bar{\nu}(\mathrm{DCl})\approx\sqrt{\frac{M_D}{M_H}}$$

$$\bar{\nu}(\mathrm{HCl})/\bar{\nu}(\mathrm{DCl})=1.41.$$

The calculated ratio $\bar{\nu}$ (HCl)/$\bar{\nu}$ (DCl) is 1.41 whereas the experimental value is $\frac{2886}{2091}=1.38$. The expected shift is 844 cm^{-1}.

Also in the case of HCN and DCN we can again approximate the ratio 1.26 yielding and expected shift of 969 cm^{-1}. The significant difference between the expected and observed value reflects the coupling between the C—H (and C—D) and the C—N vibrations.

Problem 16.4. A nuclear magnetic spectrum of a compound having the molecular formula C_2H_6OS has the following chemical shifts of proton resonance relative to water taken as zero.

Chemical shift (ppm)	*Relative intensity*	*Structure*
+1.6	3	Singlet
+2.6	2	narrow doublet
+3.3	1	narrow triplet

What is the structure of the compound?

Solution. Some possible structure may be represented as follows:

I. $HOCH_2CH_2SH$
II. CH_3OCH_2SH
III. CH_3SCH_2OH

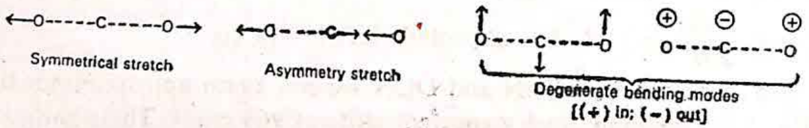
Structure I can be straightaway rejected, as there are no groups of protons having three times as many protons as any other group. The observed spectrum is too simple for this molecule and at least four peaks would be expected. Structures II and III as they contain the CH_3 group, which should appear as a singlet with the observed intensity. However, the resonance of the singlet appears farthest downfield, which makes it more likely that the CH_3 group is adjacent to a strongly deshielding atom such as oxygen. This favours the structure II. A further support to structure II comes from the fact the peak corresponding to the single proton occurs farthest upfield, suggesting that it is attached to S. The middle resonance peak corresponds to the CH_2 protons. The spin-spin patterns are in agreement with those expected for structure II.

Problem 16.5. Predict the number of vibrations and the number of infra-red absorption bands in the following molecules:

(*a*) H_2, (*b*) CO_2, (*c*) SO_2.

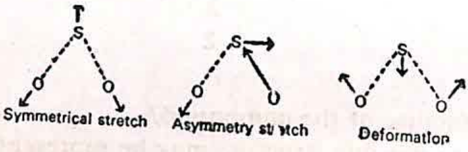
Solution. (*a*) Since H_2 is a linear diatomic molecule, there would be $3n-5=1$ vibrations in the molecule, corresponding to the H—H stretch. However, for this vibration there is no change in dipole moment and no infra-red absorption is expected.

(*b*) CO_2 is a linear triatomic molecule, there should be $3n-5=9-5=4$ fundamental vibrational modes



Only two bands are actually observed for CO_2. The symmetrical stretch does not result in a change in the dipole moment and therefore there is no infra-red band due to this mode. A band due to the asymmetrical stretch is observed. The second band corresponds to the two bending modes.

(*c*) SO_2 is non-linear, hence there should be $3n-6=3$ modes



Since all these modes produce a change in dipole moment and thus all are infra-red active.

Problem 16.6. In the infra-red spectrum of BF_3 there are three absorption bands appearing at 480, 691 and 1446 cm^{-1} which correspond to fundamental vibrations. Raman shifts of 481 and 880 cm^{-1} are observed for this compound. Using the Table 16.1, deduce the geometry of the BF_3 molecule.

Solution. A planar AB_3 molecule would have three active and two Raman active fundamentals, one of which is not observed in the infra-red spectrum. The actual data agree exactly with this prediction for a planar molecule.

Problem 16.7. Calculate the molar refraction of acetic acid (CH_3COOH). The density of acetic acid at 23°C is 1.046 g c.c.$^{-1}$. The index of refraction, n, for sodium light is 1.3715 and the molecular weight of acetic acid is 60.05 g mole^{-1}. Compare this value with the calculated value.

Solution. The observed value of the molar refraction is given according to the relation,

$$R_m = \left(\frac{n^2-1}{n^2+2}\right)\frac{M}{d}$$

$$R_m = \frac{[(1.3715)^2-1]}{[(1.3715)^2+2]}\ \frac{60.05}{1.046}$$

$$R_m = 13.03 \text{ c.c. mole}^{-1},$$

Calculated value:

$$2C = 2\times 2.418 = 4.836$$
$$4H = 4\times 1.100 = 4.400$$
$$1O^{-} = 1\times 1.525 = 1.525$$
$$1O^{-} = 1\times 2.211 = \underline{2.211}$$

$$\text{Calculated } R_m = 12.975 \text{ c.c. mole}^{-1}$$

Problem 16.8. A water solution of a coloured compound has a molar absorptivity (ϵ) of 3200 at 525 nm. Calculate the absorbance and per cent transmission of 3.40×10^{-4}F solution of 1 cm cell is used.

Solution. Absorbance, $A = \epsilon bc$

$$= 3200 \text{ litres/mole—cm} \times 1.00 \text{ cm} \times 3.4\times10^{-4} \text{ mole/litre}$$

$$A = 1.09.$$
$$A = 2 - \log T$$
$$1.09 = 2 - \log T$$
$$T = 8.1 \text{ per cent.}$$

Problem 16.9. A 1.00 g sample of steel is dissolved in nitric acid. The Mn in the sample is oxidised with KIO_3 to $KMnO_4$ and diluted to 100 ml. The absorbance reading for this solution in a 1 cm cell at the prescribed wavelength is 0.700. A 1.52×10^{-4}F solution of $KMnO_4$ served as a standard and under the same conditions absorbance was 0.350. Calculate the per cent of Mn in the steel?

Solution. $$\frac{0.700}{0.350} = \frac{C_1 \text{ (moles litre}^{-1})}{1.52\times10^{-4} \text{ moles litre}^{-1}}$$

$$= 3.04\times10^{-4}\text{M} = [KMnO_4] = [Mn]$$

$$\text{Per cent Mn} = \frac{C_1 \times \text{at. wt. of Mn} \times \text{dilution factor}}{\text{Sample weight}} \times 100$$

Per cent Mn

$$= \frac{3.04\times10^{-4}\text{ moles litre}^{-1}\times 54.94\text{ g mole}^{-1}\times 100\text{ litre}\times 100\times 100}{1.00\text{ g}\times 1000}$$

$= 0.17.$

Problem 16.10. Ten millilitres of a water sample containing a trace amount of iron is transferred to a separatory funnel. A series of standards are prepared simultaneously. Hydroxylamine hydrochloride is added to reduce the ferric ion to the ferrous state, the solutions are buffered, and bathophenthroline is added to each solution. To the solutions 6.00 ml of isoamyl alcohol (immiscible with water) is added to extract the complex Fe $(\text{bathophen})_3^{2+}$. Subsequently, the absorbance of each extract is determined at 533 nm using a 1 cm cell. From the data below calculate the concentration of iron in ppm in the original sample.

Iron conc. in water (*μg/ml*)	*Volume of solution taken* (*ml*)	*Iron conc. in isoamyl alcohol* (*μg/ml*)	*Absorbance*
0.100	10.00	0.167	0.08
0.100	20.00	0.333	0.16
1.000	5.00	0.833	0.41
1.000	10.00	1.667	0.83
1.000	20.00	3.333	1.61
Unknown	10.00		0.53

Solution. From the data above the Beer's law is linear for the system in the range of the unknown

$$\frac{A_{\text{sample}}}{A_{\text{standard}}} = \frac{C_{\text{sample}}}{C_{\text{standard}}}$$

$$C_{\text{sample}} = \left(\frac{0.54}{0.41}\right)\times 0.833\text{ g/ml}$$

$$= 1.10\ \mu\text{g/ml}.$$

The total weight of the iron in solution is, therefore, 11.0 μg and the concentration of iron in the water sample is 11.0 μg/10.00 ml or 1.10 ppm.

Problem 16.11. Given the following molar refractions:

$CH_3CH_2CH_2CH_3 = 20.6$
$CH_3CH_2OH = 12.9$
$CH_3OH = 8.3$

Calculate the value of molar refraction for $CH_3CH_2CH_2CH_2OH$.

Solution. Since molar refraction is an additive property

$$R_M\,(CH_2) = R_M\,(CH_3CH_2OH) - R_M\,(CH_3OH)$$
$$R_M\,(CH_2) = 12.9-8.3$$
$$R_M\,(CH_2) = 4.6.$$

Hence

$$R_M(CH_3CH_2CH_2CH_2OH) = R_M(CH_3CH_2OH)+2R_M(CH_2)$$
$$= 12.9+2\times 4.6$$
$$= 22.1.$$

Hence the molar refraction value for $CH_3CH_2CH_2CH_2OH$ will be 22.1.

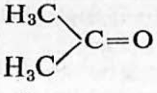
Problem 16.12. Calculate the molar refraction of acetone at 20°C. The refractive index n of acetone is 1.3591 and the density is 0.7910 g/c.c. at 20°C. The molecular weight of acetone is 58.08.

Solution. The molar refraction

$$R_M = \frac{n^2-1}{n^2+1} , \frac{M}{\rho} = \frac{(1.3591)^2-1}{(1.3591)^2+1} \cdot \frac{58.08}{0.7910}$$
$$R_M = 16.17 \text{ c.c.}$$
$$R_M = 16.17 \text{ c.c.}$$

Problem 16.13. The density of acetone is 0.7910 g cm^{-3} at 20°C, utilize the additivity of the parachor to calculate the surface tension of acetone.

Solution. The structure of acetone is



The parachor of acetone$=(3\times 7.2)+(6\times 16.2)+20.0+23.2=162.0$. The molecular weight of acetone is 58.08.

$$\frac{58.08}{0.7910} \cdot \gamma^{\frac{1}{4}} = 162.0$$
$$\gamma = 23.7 \text{ dynes cm}^{-1}.$$

Problem 16.14. A solution of L-leucine (3.0 g/50 ml of 6N HCl) had an observed rotation of +1.81° in a 20 cm polarimeter. Calculate (*a*) the specific rotation, and (*b*) the molar rotation of L-leucine (in 6N HCl).

Solution. (*a*) $[\alpha]^t_\lambda = \frac{O}{l\,c.}$

$$[\alpha]^t_\lambda = \frac{1.81}{2\times 0.06}$$
$$[\alpha]^t_\lambda = +15.1^\circ$$

(*b*) $[M]=[\alpha]^{t}_{\lambda}\times MW$

$M=(+15.1^\circ)\ (131.2)$

$M=\ +1980^\circ.$

EXERCISES

16.1. Convert the following to units of wavelength (λ) in nm.
(*o*) 6,000Å, (*b*) 30,000 Hz. [Ans. (*a*) 600 nm. (*b*) 1.0×10^{13} nm.]

16.2. Convert the following per cent *T* values of A.
(*a*) 32 per cent, (*b*) 5.4 per cent. [Ans. (*a*) 0.50, (*b*) 1.30.]

16.3. Calculate the absorbance of the solution of concentration 1.03×10^{-3} M. The molar absorptivity (ε) of the solution is 720 and pathlength is 1.0 cm. [Ans. 0.74.]

16.4. What is the energy (kJ mole^{-1} and k cal. mole^{-1}) associated with ultraviolet radiation of the wavelength.
(*i*) 184.7 nm, (*ii*) 253.7 nm, (*iii*) 366.0 nm?
[Ans. (*i*) 648 kJ mole^{-1} or 155 k cal. mole^{-1}
(*ii*) 472 kJ mole^{-1} or 113 k cal. mole^{-1}
(*iii*) 327 kJ mole^{-1} or 78.2 k cal. mole^{-1}.]

16.5. Furan has a long wavelength absorption band with $\lambda_{max}\sim250$ nm. When light of this wavelength is passed through a 10 cm cell containing a 10^{-2} M solution of furan, 20.6 per cent incident light is absorbed.
(*i*) What is the optical density (log I_0/I) of the solution?
(*ii*) What percentage of incident light is absorbed?
(*iii*) What is the molar extinction coefficient of furan at 250 nm?
(*iv*) Is the absorption likely to arise from a $\pi\rightarrow\pi^*$ transition?
[Ans. (*i*) 0.10, (*ii*) 63.1 per cent, (*iii*) 11 $\text{mole}^{-1}\ \text{cm}^{-1}$, (*iv*) No ε is too low.]

16.6. A nitrogen laser produces pulses with a peak power of 200 kW. Assuming that the pulses are rectangular in shape and have a duration of 10 ns, how many photons (λ=337 nm) are emitted in each pulse? [Ans. 3.4×10^{15}.]

16.7. The long-wavelength absorption band of benzophenone is relatively weak ($\varepsilon_{max}\sim1001\ \text{mole}^{-1}\ \text{cm}^{-1}$) and the band is shifted to shorter wavelength when the solvent is changed from cyclohexane to ethanol. For 4, 4′-bis (dimethylamino) benzophenone the long wavelength band is much stronger ($\varepsilon_{max}\sim100001\ \text{mole}^{-1}\ \text{cm}^{-1}$) and there is a solvent effect in the opposite direction. Give an explanation of these observations.
[Ans. For benzophenone the long-wavelength band arises from an $\pi\rightarrow\pi^*$ transition; for bis(dimethylamino)benzophenone the long wavelength band is $n\rightarrow n^*$.]

16.8. Riboflavine in dilute sodium acetate solution shows a maximum in the absorption spectrum at 444 mm. Calculate the energy of the corresponding electronic transition for one molecule and for one mole of riboflovine.
[Ans. $\bar{\nu}=2.25\times10^{6}\ \text{m}^{-1}$ or 22500 cm^{-1};
$\nu=6.75\times10^{14}$ Hz or 675 Tz;
$\varepsilon=4.47\times10^{-19}$ J; $\varepsilon=270$ kJ m.]

16.9. Calculate the moment of inertia of NO molecule, the internuclear distance of NO is 1.151 Å. [Ans. $I = 1.643 \times 10^{-39}$ g cm^2.]

16.10. Calculate the reduced masses of molecules in each set. Explain why those of the first set are so close to each other in magnitude (*a*) HCl, HBr, HI; (*b*) BrCl, ICl, IBr. [Ans. (*a*) 0.973 amu, 0.988 amu, 0.992 amu; (*b*) 24.6 amu, 27.7 amu, 49.0 amu.]

16.11. A compound has a molar absorptivity of 13,200 litres/mole cm at its wavelength of absorption. The absorbance for a solution of this compound in water is 0.41 using 1.0 cm cell. Calculate the concentration of the solution. [Ans. 3.1×10^{-4} M.]

16.12. A solution containing 3.0 ppm has a transmittance of 65 per cent in a 1 cm cell.

(*a*) Calculate the absorbance of the solution.

(*b*) What is the molar absorptivity of the solute if its molecular weight is 155.

(*c*) Calculate the transmittance and absorbance for a solution containing 5.2 ppm of the solute.

[Ans. (*a*) 0.19, (*b*) 9800 litres mole^{-1} cm^{-1}, (*c*) 47 per cent 0.33]

16.13. A solution containing a mixture of tetracycline and epitetracycline is found to have absorbances of 0.67 and 0.72 at 254 and 267 nm respectively. The molar absorptivities of tetracycline are 16,000 and 19,000 at 254 and 267 nm respectively, and the molar absorptivity values for epitetracycline are 16,000 and 15,000 at 254 and 267 nm respectively. Calculate the ratio of tetracycline to epitetracycline in the solution. [Ans. 1.2.]

16.14. A 10.0 mg/litre solution of procaine hydrochloride has an absorbance of 0.65 at 290 nm. (*a*) What is the concentration of the solution which has an absorbance of 0.93? (*b*) Calculate the molar absorptivity of procaine hydrochloride at 290 nm if its molecular weight is 272.8. [Ans. (*a*) 14.3 mg/litre, (*b*) 1.77×10^4 litres mole^{-1} cm^{-1}.]

16.15. A 10.0 ml sample of a $KMnO_4$ solution is titrated with 0.010F oxalic acid. The end point is detected photometrically.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightleftharpoons 2Mn^{2+} + 5CO_2 + 8H_2O$$

by monitoring the disappearance of the permanganate at 520 nm. Calculate the concentration $KMnO_4$ from the following data.

ml $H_2C_2O_4$	*A*	*ml* $H_2C_2O_4$	*A*
0.00	1.43	2.75	0.35
0.50	1.21	3.00	0.27
0.75	1.11	3.25	0.18
1.00	1.03	3.50	0.09
1.50	0.82	3.75	0.04
1.75	0.71	4.00	0.02
2.00	0.60	4.25	0.01
2.25	0.51	4.50	0.00
2.50	0.43	4.75	0.00

[Ans. 8.78×10^{-3} F.]

16.16. A sample (1.2456 g) containing sodium is dissolved, diluted to 100 ml, and analysed using the 590 nm Na line. From the data given below, determine the per cent sodium in the original sample.

Concentration of Na (mg/litre)	*Emission Reading*
0.5	24
1.0	49
2.0	103
2.5	120
4.0	190
Unknown	121

[Ans. 0.020 per cent.]

16.17. A iron sample (0.9421 g) containing a trace amount of copper is determined by atomic absorption by standard addition. The iron is dissolved in acid and diluted to exactly 100.0 ml using a volumetric flask. To 25 ml of this sample solution, 25 ml of 4.50 ppm copper solution is added. From the following data, calculate the concentration (in ppm) of the copper in the original sample.

Absorbance of sample	=0.22
Absorbance of sample with standard added	=0.31

[Ans. 263 ppm.]

16.18 If the dog has 2 quarts of blood and the fluorescence reading of 1 ml of serum is 25.7 per cent *T*, what is the total amount of teracycline in the blood?

[Ans. 89 mg.]

16.19. A solution of thiamine hydrochloride gave a fluorescence reading of 52.3 per cent *T*. Five millilitres of a standard (0.2 mg/litre thiamine HCl) were added to 5.00 ml of sample. What is the concentration of thiamine in the unknown if the fluorescence intensity of the latter solution is 67 per cent *T*?

[Ans. 0.13 mg/litre.]

16.20. The extinction coefficient $(\epsilon^{1\text{ cm}}_{1\%})$ of a glycogen-iodine complex at 450 mμ is 0.20. Calculate the concentration of glycogen in solution of the iodine complex which has an optical density of 0.38 in a 3 cm cuvette.

[Ans. 0.634 per cent.]

16.21. Calculate the concentration of ATP and TPNH in solutions with optical densities (in a 1 cm cuvette) of (*a*) 0.9 at 260 mμ and 0.15 at 340 mμ, (*b*) 0.75 at 260 mμ and 0 at 340 mμ, and (*c*) 0.531 at 260 mμ and 0.22 at 340 mμ.

[Ans. (*a*) [ATP]$=3.5\times10^{-5}$M, [TPNH]$=2.41\times10^{-5}$M;
(*b*) [ATP]$=4.87\times10^{-5}$M, [TPNH]=0;
(*c*) [ATP]=0; [TPNH]$=3.54\times10^{-5}$M.]

16.22. Ten grams of butter were saponified; the non-saponifiable fraction was extracted into 25 ml of chloroform. The optical density of the chloroform solution in a 1 cm cuvette was 0.53 at 328 mμ at 458 mμ. Calculate the carotene and vitamin A content of the butter. The extinction coefficients for carotene and vitamin A at the above two wavelengths are as follows:

Compound	$E^{1cm}_{1\%}$ in $CHCl_3$	
	328mμ	458 mμ
Carotene	340	2200
Vitamin A	1550	—0

[Ans. 2.18×10^{-4}g/100 ml. Carotene$=2.18\times10^{-4}$g/100 ml;
5.45μ g carotene/g butter $C_{\text{vit A}}=2.94\times10^{-4}$g/100 ml;
7.35μ g vitamin A/g butter.]

16.23. A suspension of bacteria containing 300 mg dry weight per litre has an optical density of 1.00 in a 1 cm cuvette at 450 mμ. What is the cell density in a suspension that has a transmission of 30 per cent in a 3 cm cuvette? [Ans. 52.2 mg/litre.]

16.24. To 2.0 ml of a glucose solution, 1.0 ml of solution containing excess of ATP, TPN^+, $MgCl_2$, hexokinase, and glucose-6-phosphate dehydrogenase was added. The optical density of the final solution increased to 0.91 at 340 mμ. Calculate the concentration of glucose in the original solution. The pathlength of the cell is 100 cm.

(Hint: The reactions that take place in solution are:

$$\text{Glucose}+\text{ATP}\xrightarrow[Mg^{2+}]{\text{hexokinase}}\text{glucose-6-phosphate}$$

$$\text{Glucose-6-phosphate}+TPN^+\xrightarrow{\text{glucose-6-phosphate dehydrogenase}}$$
$$\text{6-phosphogluconic acid-}\delta\text{-lactone}+TPNH+H^+$$

From O.D at 340 mμ, we can calculate the concentration of TPNH present. After applying the correction for dilution, the concentration of glucose in the original solution can be calculated.)

[Ans. $C_{\text{glucose}}=2.2\times10^{-4}$M.]

16.25. Calculate the change in optical density that would be observed when 2.0 ml of a solution containing lactic dehydrogenase and 10^{-4}M pyruvic acid are added to 1 cm cuvette containing 3.0 ml of a 2×10^{-4}M DPNH solution. [Ans. $\text{O.D}_{\text{original}}=1.244$
$\text{O.D}_{\text{final}}=0.497$.]

16.26. Calculate the index of refraction of chlorine gas at STP. The molar refraction for chlorine is 11.2 c.c./mole. [Ans. 1.00075.]

16.27. The molar refraction *Mr* is 1.643 for oxygen in an ether group, and is 6.818 for methane and 13.279 for dimethyl ether. Calculate the value of molar refraction for diethyl ether. [Ans. 22.915.]

16.28. The refractive index of propylene glycol at 27°C is 1.4293. Its density is 1.03 and its molecular weight is 76.1. What is its molar refraction?
[Ans. 19.06 cm³/mole.]

16.29. The molecular weight of chloroform is 119 and its density is 1.49 at 20°C. If its dielectric constant is 4.8 at 20°C. What is the molar polarisation of chloroform? [Ans. 44 63 cm³/mole.]

16.30. The index of refraction of water at 25°C is given by the equation

$$n_0^2=1.7522+\frac{8.11\times10^5}{\lambda_2^0}$$

where λ_0 is the wavelength of light in vacuum in Å. Find the wavelength of the light in water when λ_0 is 400 Å. [Ans. 2978 Å.]

16.31. Calculate the energies of three lowest vibrational states for HF for which the force constant is 9.7×10^5 dynes/cm. What is the energy spacing between these levels, and what would be the wave number of the radiation that would cause the transition from $v=0$ to the $v=1$ level?

[Ans. $\Delta\epsilon = 8.27 \times 10^{-3}$ ergs, $\bar{\nu}=4160$ cm^{-1}.]

16.32. The spacing between lines in the rotational spectrum of HCl is 20.68cm^{-1}, Calculated the bond length. [Ans. 1.29×10^{-8} cm.]

16.33 How many normal modes of vibration are possible for (*a*) HBr, (*b*) C_6H_6? (*c*) SO_2 (bent), (*d*) OCS (linear). [Ans. (*a*) 1, (*b*) 30, (*c*) 3, (*d*) 4.]

16.34. The fundamental vibration of HBr occurs at 2650 cm^{-1}. Calculate the force constant of the vibration. [Ans. 4.1×10^5 dynes/cm.]

16.35. For a static magnetic field of 14,000 gauss, what frequency of the oscillating perpendicular magnetic field will cause resonance absorption, for the following nuclei:

(*a*) ^{2}H, (*b*) ^{14}N, (*c*) ^{13}C, (*d*) ^{19}F, (*e*) ^{31}P, (*f*) ^{17}O, (*g*) ^{16}O, (*h*) ^{1}H.

[Ans. (*a*) 9.21, (*b*) 4.34, (*c*) 15.10, (*d*) 56.48, (*e*) 24.31, (*f*) 8.14, (*g*) no resonance, (*h*) 60.04 megacycles sec^{-1}.]

16.36. The molar polarization of NH_3 (g) obeys the equation $P = A + \frac{B}{T}$ where A and B have the values 5.6 and 12,000 in c c./mole respectively. Calculate the dielectric constant of NH_3 (g) at STP. [Ans. 1.00663.]

16.37. The frequency of separation of successive lines in the rotational spectrum of hydrogen chloride has been found to be 20.83 cm^{-1}. Determine the distance between the nuclei of these two atoms in the molecule.

$$\left(\text{Hint. } \Delta\nu = \frac{2h}{8\pi^2 CI} = \frac{h}{4\pi^2 CI}\right)$$

16.38. The surface tension of benzene is 22.2 dynes/cm. Calculate its parachor value. The density of benzene is 0.88 g/cm^3. [Ans. 192.4.]

19.39. An equilibrium mixture of α-and β-D-glucose has an $[\alpha]_D^{25}$ of +52.7°. Pure α-D-glucose has an $[\alpha]_D^{25}$ of + 112°. Pure β-D-glucose has an $[\alpha]_D^{25}$ of 18.7°. Calculate the proportions of α-and β-D-glucose in the equilibrium mixture. [Ans. α=36.5 per cent and β=63.5 per cent.]

16.40. A solution of D-histidine (4 g/100 ml of N HCl) had an observed rotation of−0.41° in a 20 cm polarimeter tube. Calculate (*a*) the specific rotation, and (*b*) the molar rotation of D-histidine in 1 M HCl.

[Ans. (*a*)—5.12°. (*b*) −794.6°.]

16.41. An equilibrium mixture of α-and β-D-mannose has an $[\alpha]_D^{25}$ of+14.5°, Pure α-D-mannose has an $[\alpha]_D^{25}$ of+29.3°. Pure β-D-mannose has an $[\alpha]_D^{25}$ of−16.3°. Calculate the proportions α-and β-D-mannose in equilibrium mixture. [Ans. α=67.5 per cent, β=32.5 per cent.]

16.42. The density of allyl chloride ($CH_2=CH-CH_2Cl$) is 0.938 g c.c.$^{-1}$ at 20°C Calculate the index of refraction and compare your answer with the observed value 1.4154.

16.43. The refractive index of naphthalene decahydride ($C_{10}H_{18}$) is 1.4804 at 18°C. Calculate the density and compare with the observed value of 0.895 g c.c.$^{-1}$.

16.44. The density of ethyl alcohol at 20°C is 0.789 g c.c.$^{-1}$ while that of methyl alcohol is 0.729 g c.c.$^{-1}$. Assuming that these substances form an ideal solution, calculate the refractive index of a solution containing 50 per cent by weight of each constituent. [Ans. 1.348]

16.45. The dielectric constant of CH_4 (g) at 0°C and 1 atm pressure is 1.00094. Assuming that methane behaves as an ideal gas, calculate (*i*) the induced molar polarisation, and (*ii*) the polarizability of the substance.

[Ans. (i) 7.02 cc *(ii)* 2.79×10^{-24}

16.46. The magnetic susceptibility of H_2O (l) at 25°C is—13.0×10^{-6} c.c. per mole while the density is 6.15 g pei c.c. Calculate (*i*) the specific magnetic susceptibility, and (*ii*) the magnetic permeability of liquid water at this temperature.

[Ans. (*i*) X=—0.722×10^{-6} c.c. per gram atom (*ii*) q=0.99999.]

16.47. If R_D=4.20 cm^3 for argon, find n_D for the gas at 25°C and 250 atm pressure. Assuming ideal gas laws. [Ans. 1.065.]

16.48. At 25°C the molar dielectric polarisation of a compound is measured as 58.35 cm^3, its molar refraction is 17.28 cm^3. Calculate the molecular polarizability and the dipole moment.

[Ans. $\alpha=6.85\times10^{-24}$ cm^3, μ=1.41 D.]

16.49. At 760 mm pressure the permittivity of SO_2 in the gaseus state is 1.00928 at 10°C and 1.00561 at 100°C. Find the molecular polarizability and the dipole moment. [Ans. $\alpha=4.4\times10^{-24}$ cm^3, μ=1.68 D.]

16.50. The dipole moment of the water molecule is 1.84D (6.14×10^{-30} cm). Taking the moment for each H—O bond to be 1.51 D (5.04×10^{-30} cm) with hydrogen positive, find by scale drawing or by trigonometry the angle between the two O—H bonds which would be consistent with the observed total moment. [Ans. HOH angle=105°.]

16.51. Methyl alcohol has a refractive index of 1.331 at 15°C, and its density at this temperature is 796 kg m^{-3}. Calculate the molar refraction and compare it with the value calculated from the following bond refractions.
C-H=1.69, C—O=1.51, O—H=1.88 cm^2 mol^{-1}.

[Ans. R_m=8.24 cm^3 mol^{-1}; R_m=8.46 cm^3 mol.$^{-1}$]

16.52. The dielectric constant of CH_4 (g) at 0°C and 1 atm pressure is 1.00094. Assuming that methane behaves as an ideal gas, calculate (*a*) the induced molar polarization and (*b*) the polarizability of this substance.

[Ans. (*a*) 7.02 c.c.; (*b*) 2.79×10^{-24} c.c.]

16.53. *The molar susceptibility of H_2O (l) at 25°C is—13.0×10^{-6} c.c. per mole, while the density is 0.9970 g per c.c. Find (a) the specific magnetic* susceptibility, and (*b*) the magnetic permeability of liquid water at this temperature. [Ans. (*a*) $X=0.722\times10^{-6}$ c.c. g^{-1}; (*b*) q=0.99999.]

16.54. For O_2 (g) $\chi_m=3449.0\times10^{-6}$ c.c. per mole at 25°C. Assuming α_M to ge negligible compared with χ_m, calculate the inherent magnetic moment of this molecule. [Ans. $\mu_m=2.66\times10^{-20}$ erg gauss^{-1}.]

17

NUCLEAR AND PHOTOCHEMISTRY

INTRODUCTION

The rate at which a sample containing radioactive nuclei emits particles does not depend on the chemical or physical state of the sample. In this respect, a radioactive change is quite different from a chemical reaction, whose rate is usually affected by the temperature, pressure or concentration of the reacting species. Radioactive decay is a property of the isolated nucleus. It is not stimulated by any outside effect. Various theories of nuclear structure have emerged, a liquid-drop model, a shell theory, a unified theory, a cluster theory. Nuclear structure often is described in a manner similar to atomic structure—as an assembly of protons and neutrons existing in a definite energy level analogous to the electron energy levels of the atom.

Radioactivity Decay

The decay of radioactive isotopes is a simple first order exponential process.

$$-\frac{dN}{dt} = \lambda N \qquad \ldots (1)$$

where $-\frac{dN}{dt}$ = number of atoms decaying per small increment of time

N = total number of radioactive atoms present at any given time

λ = a decay constant, different for each isotope.

The negative sign indicates at the number of radioactive atoms decrease with time

$$-\frac{dN}{dt} = \lambda N \qquad \ldots (2)$$

$$\lambda = -\frac{dN/N}{dt}$$

λ is the fraction of radioactive atoms that decays per small increment of time

$$\int_{N_0}^{N} \frac{dN}{N} = -\lambda \int_{0}^{t} dt \qquad \ldots (3)$$

where N_0 is the original number of radioactive atoms and N is the number of radioactive atoms at at any other time.

$$ln\ \frac{N_0}{N} = \lambda t \qquad \ldots (4)$$

$$2.303 \log \frac{N_0}{N} = \lambda t$$

or, in exponential form

$$N = N_0\, e^{-\lambda t} \qquad \ldots (5)$$

Half-life

The half-life of a radioactive isotope is the time required for half of the original number of atoms to decay.

$$t_{1/2} = \frac{0.693}{\lambda} \qquad \ldots (6)$$

The curie is a standard unit of radioactive decay. It is now defined as the quantity of any radioactive substance in which the decay rate is 3.700×10^{10} disintegrations per second. Specific activity refers to the amount of radioactivity per unit amount of the substance. Specific activity may be given in terms of curies per gram (c/g), millicuries per mg (mc/mg), millicuries per millimole (mc/m mole), disintegration per minute per millimole (DPM/m mole), counts per minute per micromole (CPM/μ mole) or in any other convenient way.

Isotopic Dilution Analysis

Another useful radiochemical technique is radiometric analysis, also called isotope dilution analysis. To a solution containing an unknown is added a solution containing a known quantity of a radioactive pescies isotopic with the unknown. Then the desired ion or compound is separated, and the per cent of the radioactivity recovered is determined. The non-radioactive material will have been recovered to the same per cent. The original concentration can be estimated.

Activation Analysis

Activation analysis is used to determine the traces of impurities of one element in another. The tracer technique is especially useful where quantitative recovery of the substance in question is difficult or impossible. The technique involves adding a known amount of radioactive compound to the mixture and then reisolating a small amount of the compound. The amount of compound recovered is unimportant, provided it is sufficient to weigh and count. From the specific activity of the reisolated compound as well as a total number of counts originally added, the amount of non-radioactive compound in the mixture can be calculated. Unstable or energy-rich nuclei throw off their excess energy and drop to more stable energy states by emitting various high energy particles and radiations, some nuclei split or fission in this process. These processes are called nuclear processes.

Law of Photochemical Equivalence

There are two basic laws of photochemistry. According to the first which is due to Grotthus and Draper, only light that is absorbed can produce photochemical change. The second law of photochemistry was proposed by Stark and Einstein is that a molecule absorbs a single quantum of light before it is excited or activated

$$A + h\nu \rightarrow A^*$$

Avogadro's number of photons is called an "einstein." The second law of photochemistry provides the basis for the calculation of quantum yield Φ of a particular process.

$$\Phi = \frac{\text{Number of molecules undergoing the process}}{\text{Number of quanta absorbed}}$$

The quantum yield is an efficiency rating, provides a convenient means for describing the experimental facts and helps in suggesting a mechanism for the reaction.

In photochemistry the choice of wavelength determines the quantum energy of the photons.

The effect of radiation on matter depends on the amounts of irradiation, and the measurement of the amount of irradiation is known as radiation dosimetry.

Yields of radiation induced reactions are expressed as G-values, where G is the number of molecules changed per 100 eV of energy absorbed.

The rad. The energy absorbed per unit weight of medium is known as the absorbed dose, and the official unit of absorbed dose is the rad. One rad is equal to 100 ergs per g.

The roentgen. When a sample is exposed to a beam of X-rays or γ-rays, the absorbed dose is not only dependent on the radiation but also on the properties of the medium. The unit of exposure is the roentgen R

$$1R = 2.58 \times 10^{-4} \text{ coulombs per kg.}$$

Chemical dosimetry. Chemical dosimetry is the measurement of absorbed dose by chemical means. For radiation chemists it is by far the most convenient and popular method of measuring absorbed dose. For use as a dosimetry, a chemical system must have an accurately known radiolytic yield which has previously been determined by a calorimetric method or by ionisation dosimetry. In addition, it is an advantage for the reactant or the products of irradiation to be analysed easily. If a system has a known G-value of, say, x molecules of a particular product per 100 eV of energy absorbed, then exposure of the system to radiation followed by an analysis of the product will give the amount of energy absorbed by the medium under the conditions employed.

Problem 17.1. Calculate the half-life of sodium-24 if a 24×10^{-5} g sample disintegrates at the rate of 7.73×10^{12} atoms per sec.

Solution. $$\lambda = \frac{\text{atoms disintegrating per sec}}{\text{Atoms present}}$$

$$\lambda = \frac{7.73 \times 10^{12}}{(2.4 \times 10^{-5})\left(\frac{1}{24}\right) 6.02 \times 10^{23}}$$

$$\lambda = 1.28 \times 10^{-5} \text{ sec}^{-1}.$$

$$t_{1/2} = \frac{0.693}{1.28 \times 10^{-5} \text{ sec}^{-1}}$$

$$t_{1/2} = 5.41 \times 10^{4} \text{ sec.}$$

Problem 17.2. If Co-60 has a half-life of 5.2 years how much of a 10.0 g sample will still be radioactive after 31.2 years?

Solution. Number of half lives $= \frac{31.2}{5.2}$

$= 6$

Gram sample remaining $= 100 \text{ g} \times \left(\frac{1}{2}\right)^6$

$= (10.0 \text{ g}) \times \frac{1}{64}$

$= 0.16$ g.

Problem 17.3. Calculate the radius of a nucleus of fluorine-19.

Solution. Radius $= A^{1/3}\ (1.4 \times 10^{-13} \text{ cm})$

where A is the mass number of the element

Radius $= (19)^{1/3}\ (1.4 \times 10^{-13} \text{ cm})$

Radius $= 2.7(1.4 \times 10^{-13} \text{ cm})$

Radius $= 3.8 \times 10^{-13}$ cm

The radius of fluorine nucleus will be 3.8×10^{-13} cm.

Problem 17.4. Balance the following nuclear equations and give the correct symbol for the particle designated by X in each:

(*a*) $$X + {}^{2}_{1}\text{H} \rightarrow {}^{12}_{6}\text{C} + {}^{4}_{2}\text{He}$$

(*b*) $${}^{23}_{11}\text{Na} + {}^{2}_{1}\text{H} \rightarrow {}^{24}_{11}\text{Na} + X$$

Solution. (*a*) X mass number $= (12+4)-1 = 14$

X atomic number $= (6+2)-1 = 7$

${}^{14}_{7}X$ if atomic number is 7 the element is an isotope of nitrogen ${}^{14}_{7}\text{N}$.

(*b*) X mass number $= (23+2)-24 = 1$

X atomic number $= (11+1)-11 = 1$

$$X = {}^{1}_{1}\text{H}.$$

Problem 17.5. ^{40}K constitutes 0.012 per cent of the potassium in nature. The human body contains about 0.35 per cent potassium by weight. Calculate the total radioactivity resulting from ^{40}K decay in a 75 kg human. The half-life for ^{40}K is 1.3×10^{9} years.

Solution. Total $^{40}\text{K} = 0.012\% \times 0.35\% \times 75 \times 10^{3}$ g

$$^{40}\text{K} = 3.15 \times 10^{-2} \text{ g}.$$

$$\text{Number of } ^{40}\text{K atoms} = \frac{3.15 \times 10^{-2} \text{ g}}{40 \text{ g/g atom}} \times 6.023 \times 10^{23} \text{ atoms/g atm}$$

$$= 4.75 \times 10^{20} \text{ atoms}$$

$$\lambda = \frac{0.693}{1.3 \times 10^{9} \times 365 \times 24 \times 60}$$

$$\lambda = \frac{6.93 \times 10^{-1}}{6.83 \times 10^{14}} \text{min}^{-1}$$

$$\lambda = 1.014 \times 10^{-15} \text{ min}^{-1}$$

$$-dN/dt = \lambda . N.$$

$$\text{DPM} = (1.014 \times 10^{-15})(4.75 \times 10^{20})$$

$$\text{DPM} = 4.82 \times 10^{-5} \text{ DPM}.$$

Problem 17.6. A solution contains 1 mc of L-phenyl alanine C^{14} (uniformly labelled) in 2.0 ml of solution. The specific activity of the labelled amino acid is given as 150 mc/m mole. Calculate (*a*) the concentration of L-phenylalanine in the solution and (*b*) the activity of the solution in terms of CPM/ml at a counting efficiency of 80 per cent.

Solution. (*a*) If 1 m mole is equivalent to 150 mc, calculate the number of m moles that corresponds to 1 mc:

$$\frac{1 \text{ m mole}}{150 \text{ mc}} = 0.00667 \text{ m mole/mc.}$$

The 1 mc is dissolved in 2.0 ml

$$\therefore \text{ Concentration} = \frac{6.67 \times 10^{-3} \text{ m mole}}{2.0 \text{ ml}}$$

$$\text{Concentration} = 3.335 \times 10^{-3} \text{ m moles/ml}$$

$$\text{Concentration} = 3.335 \times 10^{-3} \text{ M}$$

(*b*) 1 curie $= 2.22 \times 10^{12}$ DPM

1 mc $= 2.22 \times 10^{9}$ DPM

Total activity $= (0.80)\,(2.22 \times 10^{9})$ CPM

Total activity $= 1.775 \times 10^{9}$ CPM in 20 ml

$$\frac{1.775 \times 10^{9} \text{ CPM}}{2.0 \text{ ml}} = 0.888 \times 10^{9} \text{ CPM/ml}$$

$$\text{activity} = 8.88 \times 10^{8} \text{ CPM/ml.}$$

Problem 17.7. Calculate the energy change in k. cal. for the fission of one mole of $^{239}_{94}\text{Pu}$ by the reaction

$$^{239}_{94}\text{Pu} + {}^{1}_{0}n \rightarrow {}^{90}_{38}\text{Sr} \pm {}^{146}_{58}\text{Ce} + 4\ {}^{1}_{0}n + 2\ {}^{0}_{-1}\text{e}$$

given the observed masses of the various isotopes are $^{239}_{94}\text{Pu}$ (239.0006), $^{90}_{38}\text{Sr}$ (89.8864), $^{146}_{58}\text{Ce}$ (145.8865), $^{1}_{0}n$ (1.00867) and $^{0}_{-1}e$ (0.000549).

Solution (*a*) Product mass: 89.8864 $^{90}_{38}\text{Sr}$

$$+145.8865\,{}^{145}_{58}\text{Ce}$$

$$+4(1.00867)\ 4.03468\ 4\ {}^{0}_{1}n$$

$$+2(0.000549)\ 0.00110.2\ {}^{0}_{1\text{-}}e$$

$$\overline{\underline{239.80868}}$$

Reactant mass: 239.0006 $^{239}_{94}Pu$

$$\begin{array}{l} +1.008671 \ ^{1}_{0}n \\ \hline 240.000927 \\ \hline \end{array}$$

$\Delta m = 240.00927 - 239.80868 = 0.20059$

This loss in mass is converted to energy that is released, i.e., the reaction is exothermic. The energy released is

$$X_{k.cal} = 0.20059 \text{ g} \times \frac{2.15 \times 10^{10} \text{ k. cal}}{1 \text{ g}} = 4.31 \times 10^{9} \text{ k. cal.}$$

Problem 17.8. Calculate the energy released in joules and in MeV in the following nuclear reactions:

(*a*) $^{2}_{1}H + ^{2}_{1}H \rightarrow ^{3}_{2}He + ^{1}_{0}n$

(*b*) $^{2}_{1}H + ^{3}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$

Assume that the mass of $^{2}_{1}H$ is 2.0141, mass of $^{3}_{1}H$ is 3.0160, mass of $^{4}_{2}He$ is 4.0015, mass of $^{3}_{2}He$ is 3.0160.

Solution. Mass of $^{2}_{1}H$ atom $= 2.0141$ amu

Mass of $^{3}_{1}H$ atom $= 3.0160$ amu

Mass of $^{3}_{2}He$ atom $= 3.0160$ amu

Mass of $^{4}_{2}He$ atom $= 4.0026$ amu

Mass of neutron $= 1.0087$ amu.

In these reactions there is no change in the total number of external electrons, and the difference in isotopic masses is the same as the difference in nuclear masses.

(*a*) $^{2}_{1}H + ^{2}_{1}H \rightarrow ^{3}_{2}He + n$

Mass consumed in reaction$=2.0141+2.0141-0.0160-1.008$

$=0.0035$ amu

Energy released in reaction$=mc^2$

$$=0.0035 \text{ amu} \times \frac{1.66\times10^{-27}}{1 \text{ amu}}\text{kg}\left(3.00\times10^{8} \ \frac{\text{m}}{\text{sec}}\right)^2$$

$$=5.2\times10^{-13}\text{J}$$

$$5.2\times10^{-13}\text{ J}\times\frac{1\text{ eV}}{1.60\times10^{-19}\text{ J}}\times\frac{1\text{ MeV}}{1\times10^{6}\text{ eV}}$$

$$=3.25\text{ MeV}$$

(*b*) ${}^{2}_{1}\text{H}+{}^{1}_{3}\text{H}\rightarrow{}^{4}_{2}\text{He}+n$

Mass consumed in reaction$=2.0141+3.0160-4.0026-1.0087$

$=0.0188$ amu

Energy released in reaction$=mc^2$

$$=0.0188\text{ amu}\times\frac{1.66\times10^{-27}\text{ kg}}{1\text{ amu}}\times(3.00\times10^{8}\text{ m. sec}^{-1})^2$$

$$=2.81\times10^{-12}\text{ J}$$

$$2.81\times10^{-12}\text{ J}\times\frac{1\text{ eV}}{1.60\times10^{-19}\text{ J}}\times\frac{1\text{ MeV}}{1\times10^{6}\text{ eV}}$$

$$=17.6\text{ MeV.}$$

Problem 17.9. ${}^{239}_{94}\text{Pu}$ is an alpha particle emitter. Calculate its half-life if a 0.100 mg sample produces 1.40×10^{7} disintegrations per minute.

Solution. Atoms disintegrating in unit time

$=\lambda A=1.40\times10^{7}$ atoms/min

A=total number of atoms

$$A=0.100\text{ mg}\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{1\text{ mole}}{239\text{ g}}\times\frac{6.02\times10^{23}\text{ atoms}}{1\text{ mole}}$$

$$A=2.52\times10^{17}\text{ atoms}$$

$$\lambda=\frac{1.40\times10^{7}\text{ atoms/min}}{2.52\times10^{17}\text{ atoms}}$$

$$\lambda=5.56\times11^{-11}\text{ min}^{-1}$$

$$t_{1/2}=\frac{0.693}{\lambda}=\frac{0.693}{5.56\times10^{-11}\text{ min}^{-1}}$$

$$t_{1/2}=1.25\times10^{10}\text{ min}$$

$$t_{1/2}\text{ in years}=1.25\times10^{10}\text{ min.}\times\frac{1\text{ hr}}{60\text{ min}}\times\frac{1\text{ day}}{24\text{ hr}}\times\frac{1\text{ year}}{365\text{ days}}$$

$t_{1/2}$ in years$=2.38\times10^{4}$ years.

Problem 17.10. To 50.00 ml of a solution containing an unknown concentration of zinc ion was added 0.100 μ curie of $^{62}Zn^{2+}$ in 10 ml of solution, and the total volume was diluted to 100 ml with water. Precipitation of a zinc salt yielded 0.200 g of zinc in the solid phase, with an activity of 0.823 μ curie. What was the original concentration of the zinc ion?

Solution. Per cent Zn recovered=per cent ^{62}Zn recovered

$$= \frac{0.0823}{0.100} \times 100$$

$$= 82.3 \text{ per cent}$$

$$\text{Total zinc} = \frac{0.200 \text{ g recovered}}{0.883 \text{ g recovered/g total}}$$

$$\text{Total zinc} = 0.243 \text{ g total}$$

$$\frac{0.243 \text{ g}}{(65.37 \text{ g/mole})\,(0.0500 \text{ litre})} = 0.0743 \text{ M } Zn^{2+}$$

Problem 17.11. Determine the magnitude of an einstein for red light of wavelength 6500 Å.

Solution. $$\triangle E = \frac{Nhc}{\lambda}$$

$$\triangle E = \frac{(6.022 \times 10^{23})\,(6.626 \times 10^{-34})\,(3.00 \times 10^{8})}{6.50 \times 10^{-7}}$$

$$\triangle E = 1.84 \times 10^{5} \text{ J einstein}^{-1}.$$

Problem 17.12. In a certain experiment irradiation of biacetyl gas with UV radiation (253.7 nm) for 1.80×10^{4}s produced 6.33×10^{-8} mole cm^{-3} of CO. The intensity of the radiation absorbed by the biacetyl was 1.71×10^{-6} J cm^{-3} s^{-1}. What is the quantum yield of CO?

Solution. Energy of one photon, $E = \dfrac{hc}{\lambda}$

$$= \frac{(6.63 \times 10^{-34})\,(3.00 \times 10^{8})}{253.7 \times 10^{-9}}$$

$$= 2.18 \times 10^{12} \text{ cm}^{3} \text{ s}^{-1}$$

The number of photons absorbed is

$$I_{at} = (2.18 \times 10^{12})\,(1.80 \times 10^{4}) \text{ cm}^{-3} = 3.93 \times 10^{16} \text{ cm}^{-3}$$

Number of CO molecules

$$6.33 \times 10^{-8} \times N = (6.33 \times 10^{-8})\,(6.02 \times 10^{23}) \text{ cm}^{-3}$$

$$= 3.81 \times 10^{16} \text{ cm}^{-3}$$

$$\Phi = \frac{3.81 \times 10^{16}}{3.93 \times 10^{16}} = 0.97.$$

Problem 17.13. When ergosterol is irradiated with ultraviolet light below 3100 Å, Vitamin D, the antirachitic Vitamin is produced in proportion to the number of quanta absorbed. When irradiated ergosterol was included in diet otherwise devoid of vitamin D, it was found that absorbed radiant energy of about 750 ergs was necessary to prevent rickets in a rat when fed over a period of 2 weeks. The light used had a wavelength of 2650 Å.

Solution. (*a*) The number of quanta necessary to give 750 ergs?

$$E=h\nu=\frac{(6.62\times10^{-27})\,(3.0\times10^{10})}{2.65\times10^{-5}}=7.5\times10^{-12}\text{ erg}$$

$$\text{Number of quanta}=\frac{750}{7.5\times10^{-12}}=1.0\times10^{14}$$

(*b*) If we assume that the primary photoprocess is the only chemical reaction, how many molecules of vitamin D per day are necessary to prevent rickets in a rat?

$$\text{Molecules per day}=\frac{1.00\times10^{14}}{14}=7.14\times10^{12}$$

(*c*) If vitamin D has a molecular weight of the same order of magnitude as ergosterol (382), how many grams of vitamin D per day are necessary to prevent rickets in a rat?

$$\text{Grams per day}=\frac{(7.14\times10^{12})\,(382)}{6.02\times10^{23}}$$

$$=4.53\times10^{-9}.$$

EXERCISES

17.1. Classify each of the following nuclides as "probably stable," "beta emitters" or "positron emitters," $^{49}_{20}$Ca $^{195}_{80}$Hg $^{208}_{82}$Pb, $^{8}_{5}$B $^{150}_{67}$Ho, $^{30}_{13}$Al, $^{120}_{50}$Sn, $^{94}_{36}$Kr.

[Ans. Beta emitter: $^{40}_{20}$Ca, $^{30}_{13}$Al, $^{94}_{36}$Kr

Positron emitter: $^{8}_{5}$B, $^{150}_{67}$Ho, $^{195}_{80}$Hg

Stable: $^{208}_{82}$Pb, $^{120}_{80}$Sn.]

17.2. Of the following nuclides $^{114}_{48}$Cd, $^{114}_{49}$In and $^{114}_{50}$ Sn which is likely to be radioactive? [Ans. $^{111}_{49}$In.]

17.3. The half-life of $^{212}_{82}$ Pb is 10.6 hours that of its daughter $^{212}_{83}$Bi is 60.5 minutes. How long will it take for a maximum daughter activity to grow in freshly separated $^{212}_{82}Pb$? [Ans. 3.78 hours.]

17.4. Some radioactive material is decaying with a 30-day half-life. Chemical separation procedures yield two fractions. Immediately after separation one of the fractions decays within a 2 days-life. Would the other fraction show immediately after separation, constant activity, increasing activity, decay with a 30 day half, or decay with a 28 day half-life? Explain.

[Ans. Increasing activity.]

17.5. A sample of rock from Grand Canyon was analysed for gold content by neutrons activation. A 1.00 gram sample was irradiated in a flux of 10^{12} neutrons/cm^2 sec for about 3 weeks. Then the sample was removed, dissolved and some inactive gold carrier was added. Gold was precipitated as the sulphide and was found to have an activity due to $^{192}_{79}Au$ of 50 dis/min, corrected to the time of bombardment. The cross-section of $^{198}_{79}Au$ for neutrons is 98 barns. The half-life of $^{198}_{79}Au$ is 2.7 days. What weight of gold is there per gram of rock sample? [Ans. 1×10^{-9} gram.]

17.6. Ca^{45} has a half-life of 163 days. Calculate (*a*) the decay constant (λ) in terms of days^{-1} and sec^{-1}, and (*b*) the per cent of initial radioactivity remaining in a sample after 90 days.

[Ans. $\lambda = 4.26 \times 10^{-3}$ days^{-1}, 4.92×10^{-8} sec^{-1}, 68.1 per cent.]

17.7. I^{131} has a half-life of 8 days. Calculate (*a*) the fraction of the I^{131} atoms that decays per day per minute, and (*b*) the specific activity of pure I^{131} in terms of DPM/g, curries/g and curries/g atom.

[Ans. (*a*) One atom out of every 11.5 radioactive atoms present decays per day, one atom out of every 16,600 radioactive atoms present decays per minute, (*b*) 27.65×10^{16} DPM/g, 12.45×10^4 curries/g 950 curies/g atom.]

17.8. Calculate the number of atoms disintegrating per minute in a mass of 0.001 g of radium which is an alpha emitter with a half-life of 1620 years,

[Ans. 1.85×10^{10}.]

17.9. The isotope of $^{60}_{27}Co$ has a half-life of 5.27 years. What amount of a 0.0100 g sample of $^{60}_{27}Co$ remains after 1.00 year? [Ans. 0.0088 g.]

17.10. The nuclide $^{198}_{79}Au$ has a half-life of 64.8 hours. How much of a 0.0100 g sample remains at the end of one day? [Ans. 7.7×10^{-3} g.]

17.11. By natural radioactivity $^{238}_{92}U$ undergoes the following changes

$^{236}_{92}U \rightarrow UX_1$ (α-particle)

$UX_1 \rightarrow UX_2$(β-particle).

Determine the atomic mass and atomic number of UX_1 and UX_2.
[Ans. UX_1 mass number 234, atomic number 90; UX_2 mass number 234, atomic number 91.]

17.12. On analysis a sample of uranium ore was found to contain 0.277 g of $^{206}_{82}Pb$ and 1.067 g of $^{238}_{92}U$. The half-life period of uranium is 4.51×10^9 years. If all lead were assumed to have come from decay of $^{238}_{92}U$, what is the age of the ore? [Ans. 1.22×10^9 years.]

17.13. After the lapse of half an hour only 1/4th of the initial quantity of a radioisotope remains behind. Calculate its disintegration constant and its half-life. [Ans. $k = 1.396\ \text{hr}^{-1}$, Half-life 10.5 hour.]

17.14. A sample of pitch blende is found to contain 50 per cent uranium and 2.425 per cent lead. Of this lead only 93 per cent was ^{206}Pb isotope. If the disintegration constant is $1.52 \times 10^{-10}\ \text{year}^{-1}$, how old could be the pitch blend deposit? [Ans. 3.33×10^8 years.]

17.15. A wooden idol recovered in an excavation was found to contain 25.6 per cent as much C^{14} as ordinary wood todate has. What is the approximate age of this wooden idol? [Ans. 11,330 years.]

17.16. The half-life of ^{100}Tc, a β-emitter is 16 sec. How many atoms of $^{100}\Gamma_c$ are present in a sample with an activity of 0.200 μ_c? What is the weight of the sample? [Ans. 2.84×10^{-19} g T_e.]

17.17. The nuclide $^{213}_{85}At$ decays to $^{209}_{83}Bi$ by alpha emission. The mass of $^{213}_{85}At$ is 212.9931 u and the mass of $^{209}_{83}Bi$ is 208.9804 u. Calculate the energy released in this process. [Ans. 9.46 MeV.]

17.18. The energy released by decay of $^{27}_{14}Si$ by positron emission is 3.80 MeV. The daughter nuclide $^{27}_{13}Al$ has a mass of 26.98174 u. What is mass of $^{27}_{14}Si$? [Ans. 26.98672 u.]

17.19. Calculate the weight in grams of calcium in 1 mc of Ca^{45}. The half-life of Ca^{45} is 163 days. [Ans. 5.62×10^{-3} g.]

17.20. A 10 ml suspension of Cr^{51} labelled red blood cells containing 3×10^8 CPM total radioactivity was injected into an animal. After 10 minutes a small blood sample was taken and found to contain 5×10^4 CPM/ml. Calculate the total blood volume of the animal. [Ans. 6 litre]

17.21. The carbon from the heartwood of a giant sequsia tree give 10.8 $^{14}_{6}C$ counts per minute per gram of carbon, whereas the wood from the outer portion of the tree gives 15.3 $^{14}_{6}C$ counts per minute per gram of carbon.

How old is the tree? [Ans. 2890 years.]

17.22 Write the balanced nuclear reactions for the following:

(*a*) The decay of ${}^{36}_{17}$Cl by beta emission.

(*b*) The decay of ${}^{13}_{7}$N by positron emission.

(*c*) The decay of ${}^{230}_{90}$Th by alpha emission.

[Ans. (*a*) ${}^{36}_{17}\text{Cl} \rightarrow {}^{36}_{18}\text{Ar} + {}^{0}_{-1}\text{e}$

(*b*) ${}^{13}_{7}\text{C} \rightarrow {}^{13}_{6}\text{C} + {}^{0}_{-1}\text{e}$

(*c*) ${}^{230}_{90}\text{Th} \rightarrow {}^{226}_{88}\text{Ra} + {}^{4}_{2}\text{He}$.]

17.23. Predict whether the following unstable nuclei would decay by beta or positron emission; (*a*) ${}^{9}_{3}$Li, (*b*) ${}^{20}_{11}$Na, (*c*) ${}^{35}_{18}$Ar, (*d*) ${}^{32}_{15}$P.

[Ans. (*a*) beta, (*b*) positron, (*c*) positron, (*d*) beta.]

17.24. What is the mass of the nucleus ^{14}C if 0.60 MeV of energy is liberated in the reaction

$${}^{14}_{7}\text{N} + n \rightarrow {}^{14}_{6}\text{C} + p$$

The mass of ${}^{14}_{7}$N is 14.003074 amu. [Ans. 13.99998 amu.]

17.25. Assume that a reaction that may be used in a hydrogen bomb is ${}^{6}_{3}\text{Li} + {}^{2}_{1}\text{H} \rightarrow 2\,{}^{4}_{2}\text{He}$. From the mass difference in the reactants and products, calculate the number of kilo joules produced when 100 g of lithium reacts by this process. Isotopic masses, ${}^{6}_{3}$Li, 6.025126; ${}^{2}_{1}$H, 2.014102; ${}^{4}_{2}$He, 4.00260 atomic mass units. [Ans. 3.60×10^{10} kJ.]

17.26. If the average loss on ion-pair formation in a gas is 35 eV, how many ion pairs are formed in a gas by the passage of 5.3 MeV alpha particle? [Ans. 1.5×10^{5} years.]

17.27. Bombardment of ^{52}Cr with high energy alpha particles yields two products *A* and *B* according to the equation

$$2\,{}^{52}_{24}\text{Cr} + 2\,{}^{4}_{2}\text{He} \rightarrow A + B + {}^{1}_{1}\text{H} + 7\,{}^{1}_{0}n$$

A then emits a positron to become *B* and *B* emits a positron to become ${}^{52}_{24}$Cr. Identify *A* and *B* and write equations for the various reactions.

[Ans. $A = {}^{52}_{26}\text{Fe}$; $B = {}^{52}_{25}\text{Mn}$

$${}^{52}_{26}\text{Fe} \rightarrow {}^{52}_{26}\text{Mn} + {}^{0}_{1}\text{e}$$

$${}^{52}_{25}\text{Mn} \rightarrow {}^{52}_{24}\text{Cr} + {}^{0}_{1}\text{e}$$]

17.28. Balance the following equations and give the correct symbol for the particle designated by X in each

(*a*) ${}^{27}_{13}\text{Al} + X \rightarrow {}^{24}_{11}\text{Na} + {}^{4}_{2}\text{He}$

(*b*) ${}^{235}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{141}_{56}\text{Ba} + 3\,{}^{1}_{0}n + X$

[Ans. (*a*) $X = {}^{1}_{0}n$, (*b*) $X = {}^{92}_{36}\text{Kr}$.]

17.29. A solution of L-lysine-C^{14} (uniformly labelled) contains 1.2 mc and 0.77 mg of L-lysine per ml. Calculate the specific activity of lysine in terms of (*a*) mc/mg, (*b*) mc/m mole, (*c*) DPM/μ mole, and (*d*) CPM/μ mole for carbon at a counting efficiency of 80 per cent.

[Ans. (*a*) 1.56 mc/mg, (*b*) 228 mc/m mole, (*c*) 5.06×10^8 DPM/μ mole (*d*) 6.75×10^7 CPM/μ mole of carbon.]

17.30. Fifty-six μg of Co^{60} labelled vitamin B_{12} containing 7.39×10^5 CPM, were added to a sample containing an unknown amount of unlabelled vitamin B_{12}. The sample was then extracted with vitamin B_{12} purified by chromatography. The final product contained 49μ g of vitamin B_{12} and 1.58×10^5 CPM of radioactivity. Calculate the amount of unlabelled vitamin B_{12} in the sample. [Ans. 172.5μ g.]

17.31. An isotope with a half-life of 10 hours was injected into the blood-stream of an animal. Blood samples were taken periodically and counted immediately. The specific activities of the sample are shown below. From the data, calculate the biological half-life of the isotope in the blood stream.

Sample time (hours)	*Specific activity (CPM/ml)*
2	9400
4	6490
6	4490
10	2140
18	490

[Ans. Biological $t_{\frac{1}{2}}$ = 6 hour, effective $t_{\frac{1}{2}}$ = 3.75 hour; CPM/ml at zero time = 13,600.]

17.32. Atmospheric oxygen contains 99.7587 per cent of ^{16}O, 0.0374 per cent of ^{17}O and 0.2039 per cent ^{18}O. Calculate the average atomic weight of oxygen from air, if the atomic masses of the isotopes are 15.9949, 16.9991 and 17.9992 respectively. [Ans. 15.9994 amu.]

17.33. Naturally occurring neon is a mixture of three neon isotopes, ^{20}Ne, ^{21}Ne and ^{22}Ne. It has been found to have 90.4 per cent ^{20}Ne, 0.5 per cent ^{21}Ne and 9.0 ^{22}Ne. Calculate the expected atomic weight of neon.

[Ans. 20.0 amu.]

17.34. Determine the momentum of a photon of violet light having a wavelength 3950 Å.

[Ans. 1.68×10^{-27} kg.m. s^{-1}.]

17.35. The quantum yield for a particular photochemical reaction is 0.5. What wavelength of light is necessary to overcome a free energy barrier of —763 kJ per mole of reactant molecule and cause this reaction to occur?

[Ans. 3.13×10^{-7} m.]

17.36. The quantum yield for the photochemical reaction

$$(CH_3)_2\,CO \rightarrow C_2H_6 + CO$$

is 0.2. For how long must light of intensity 6.29×10^{17} quanta-s^{-1} be incident on the sample to produce 0.01 moles CO gas. Assume that 85 per cent of the light is absorbed by the sample.

[Ans. 15.6 hour.]

17.37. In the photochemical reaction

$$NH_3(g) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)$$

with light at wavelength 2.10×10^{-7} m, it is found that 1.94 kJ of energy decomposes 7.5×10^{-4} moles of NH_3. Calculate the quantum yield?

[Ans. 0.22.]

17.38. A solution placed in 1.0 cm solution cell is found to transmit 34.3 per cent of light at wavelength 2.16×10^{-7} m. The molar absorption coefficient for the solute at this wavelength is 6.73×10^4 m^{-1} cm^{-1}. What is the concentration of the solution? Assume that the per cent transmittance given above has been corrected for any absorption due to solvent.

[Ans. 1.59×10^{-5} M]

17.39. The dye acriflavine, when dissolved in water, has its maximum light absorption at 4530 Å, and its maximum fluorescence emission at 5080 Å. The number of fluorescence quanta is, on the average, 53 per cent of the number of quanta absorbed. Using the wavelengths of maximum absorption and emission, what percentage of absorbed energy is emitted as fluorescence?

[Ans. 47 per cent.]

17.40. In a measurement of the quantum efficiency of photosynthesis in green plants, it was found that 8 quanta of red light at 6850 Å were needed to evolve one molecule of O_2. The average storage in the photosynthetic process is 112 k. cal. per mole of O_2 evolved. What is the energy conversion efficiency in this experiment?

[Ans. 34 per cent.]

17.41. An acid solution of $K_3[Fe(C_2O_4)_3]$ is used as an actinometer to measure the intensity of the light incident upon a vessel. After exposure to light of wavelength 253.7 nm for 10^3 s, the concentration of ferrous iron was found to be 5.0×10^{-5} M. The fraction of light absorbed by actinometer solution is 0.1. What is the intensity of the incident light?

[Ans. 1.89×10^{-5} J cm^{-3} s^{-1}.]

17.42. An aqueous solution of monochloroacetic acid decomposes photochemically as follows:

$$ClCH_2CO_2H + H_2O \rightarrow HOCH_3CO_2H + HCl$$

Photolysis of 8.23 ml samples at 2537 Å, 25°C, and an initial monochloroacetic acid concentration of 0.5 M, yielded the following results for two different exposure times, *t*

t/(*min*).	*837*	*2774*
absorbed energy (10^8 erg)	3.436	1.190
amount of Cl^- (10^{-5} mole)	2.325	0.863

Separate experiments in the dark showed that 3.5×10^{10} mole Cl^{-1} min^{-1} is found thermally. Calculate quantum yield of the photochemical reaction. **[Ans. 0.31.]**

17.43. Samples of (*a*) aniline, and (*b*) cyclohexane are exposed to 10^5 roentgens of X-rays of effective mean energy 100 keV. Calculate the dose in rads for each. **[Ans. (*a*) 86000 rads, (*b*) 91000 rads.]**

17.44. The irradiation of an aromatic solution produces solvent triplets in a yield, independent of solute concentration, of $G=40$, with a mean life in the pure solvent of 1.4×10^{-7} s, what would be the yield of solute triplets if the solvent triplets could transfer energy to solute wiih $k=10^{10}$ m^{-1} s^{-1} (*a*) for 1.25×10^{-4} M solution, (*b*) for 10^{-3} M solution? **[Ans. (*a*) $G=0.6$, (*b*) $G=2$ 3.]**

17.45. Using a cell 1 cm in thickness, the following data for K_2CrO_4 solution were obtained at $\lambda = 3660$ Å in a photo-electric calorimeter

$\frac{I_t}{I_o}$	*Concentration* (*moles/litre* $\times 10^4$)
0.420	0.80
0.275	1.20
0.175	1.60
0.110	2.00

Plot these data and determine the molar absorption and extinction coefficient of K_2CrO_4 at this wavelength.

18

MATHEMATICAL METHODS

INTRODUCTION

In order to improve communication across interdisciplinary and international boundaries, international scientific organizations are engaged in working out standardized names, symbols and units for physicochemical quantities. One such organization is International Union of Pure and Applied Chemistry (IUPAC).

The SI units were adopted by the General Conference of Weights and Measures in 1960 for use in Science and Technology. When the chemist measures any physical quantity, he counts these units on the scale of whatever piece of equipment he happens to be using, he gets a number represented by a certain figure which he writes down. However, he tries to estimate the smallest possible fraction of the scale unit. The idea of significant figures is based on the fact that it is possible to read a scale just so accurately and no more. In reading scales you can generally make a visual estimate of 0.1 the smallest unit, if the unit is not too small. Again if each centimetre is marked into ten units each one of these is 0.1 cm. This means that the best visual estimate that can be made is 0.1×0.1 or 0.01 cm. This is considered as probable error in each measurement regardless of its total length. For example, in measuring the height $h=0.47$ cm, it is possibly as large as 0.48 cm or as small as 0.46 cm. Such a value is often writen as 0.47 ± 0.01. Since both the 4 and 7 are known with some degree of certainty, this number is said to have two significant figures. There would still be two significant figures if the uncertainty were as large as 0.40 ± 0.04. The zeros before the decimal point are never considered significant.

The percentage error depends on the size of the measurement as under:

$$\text{Percentage error} = \frac{\text{Error in the quantity}}{\text{The quantity}} \times 100 \text{ per cent}$$

The per cent error in the measured height 0.47 ± 0.04 can be calculated as

$$\text{Per cent error} = \frac{0.04}{0.47} \times 100$$
$$= 8.51 \text{ per cent.}$$

Scientific Notation

The scientific notation is also known as the powers of ten method. It is used by chemists for two reasons. First, it indicates the degree of precision of the numbers used in calculation. Second it avoids errors arising from the use of "bulky" numbers which have large number of zeros before or after the decimal point. In order to write a number in scientific notation the following points should be borne in mind.

Rule I. Move the decimal point in each number to the position behind the first non-zero digit, giving a number between 1 and 10. If the number is less than one, do just as before, but use a negative exponent. The following examples will illustrate the method

(*a*) 3867.5.

Since this number is greater than 1 and the number of moves is 3. The number can be written as 3.8675×10^3.

(*b*) 0.0481.

This number being less than one and we have to make two moves, the number can thus be written as 4.81×10^{-2}.

Rule II. Multiply and divide the numbers and their powers of 10 separately. The following examples will illustrate the rule.

(*a*) $(3.0675 \times 10^3)(4.91 \times 10^{-2})$

$$= 15.10 \times 10^{3-2}$$
$$= 15.10 \times 10^{1}$$

or
$$= 1.51 \times 10^{2}.$$

the exponents are added in multiplication.

(*b*)
$$\frac{3.0675 \times 10^{3-2}}{4.91 \times 10^{-2}}$$
$$= 0.624 \times 10^{3-(-2)}$$
$$= 0.624 \times 10^{5}$$
$$= 6.24 \times 10^{4}$$

Exponents and Exponential Notation

When two or more quantities are multiplied together, the combination is called a product. Sometimes in a product a number or a quantity is repeated. For example, the product 3.3.8 contains a repeated 3, the product $n \times n \times n$ contains a repeated n. In products, repeated quantities such as these can be conveniently represented by exponents. The exponent is equal to the number of times a quantity is repeated.

The quantity 3.3 is equivalent to 3^2 and the $n \times n \times n$ is equivalent to n^3. These quantities may be described as three squared or n cubed. Exponential notation consists of a number or quantity written with a superscript. The number or quantity is called the base; the superscript is the exponent or power to which the base is raised. In n^3, n is the base and 3 power is called the exponent. The following systematic procedure called the laws of exponents are found to be very useful.

Law I. $b^k . b^l = b^{k+l}$

Law II. $(b^l)^m = b^{lm}$

Law III. $(ac)^j = a^j c^j$

Law IV. $\frac{A^k}{a^j} = a^{k-j}$

Logarithms

Normally chemical calculations use base 10 logarithms. These logarithms are exponents of 10. Logarithms consist of a whole number called characteristic, this is followed by a decimal number called mantissa. For finding the logarithm of a number, following procedure will be useful.

(*a*) Let the number be 343.

1. Write the given number in the scientific notation that is as the product of some number and some power of 10, i.e.,

$$343 = 3.43 \times 10^2$$

2. Look up the logarithm of the number preceding the power of 10 in a log table. Log 3.43=0.5353.

3. Add this to the exponent of 10. Thus

$$\text{Log } 343 = 0.5353 + 2 = 2.5353.$$

(*b*) Let the number be 0.020. The log of this number will be negative:

1. $0.0200 = 2.00 \times 10^{-2}$.
2. Log 2.00=0.3010.
3. Log 0.020=0.3010−2.

To find a number from its logarithm, following step should be adopted.

1. Make sure that log is written in a form such that the decimal part is positive.

Let the number has the logarithm −4.3010. Add the log to the next largest whole number, then subtract that number, i.e.,

$$(-4.3010 + 5) - 5 = 0.6990 - 5.$$

2. Look up the mantissa in the logarithmic part of the table and find the number to which it closely corresponds. For example, the

number 5.00 corresponds to 0.6990 in the mantissa part of the table.

3. Write this number as the first part of the scientific notation. Then use the whole number in the log as the exponent of 10. For example in this case

$$0.6990-5$$
$$5.00\times 10^{-5}.$$

The Method of Least Square

This is a statistical method and makes use of the principle that the most probable true value of an observed quantity is that value for which the sum of the squares of the deviations from it is at a minimum.

Let y and x be the values determined experimentally in n trials. This gives us n pairs of values of y and x. If y and x are related by the equation,

$$y=mx+b \qquad \ldots (1)$$

We are interested to find the best values for m and b consistent with the experimental data. Let r be the deviation defined as,

$$r=y-(mx+b) \qquad \ldots (2)$$

For n trials we can write after squaring,

$$\Sigma r^2=\Sigma y^2+m^2\,\Sigma x^2+nb^2-2m\,\Sigma xy-2b\,\Sigma y+2mb\,\Sigma x \qquad \ldots (3)$$

The best values for m and b are found by minimizing Σr^2 with respect to m and b. This can be achieved by setting the first derivatives of r^2 with respect to m and b respectively equal to zero, i.e.,

$$\frac{\partial \Sigma r^2}{\partial m}=2.m\sum x^2-2\sum xy+2b\sum x=0 \qquad \ldots (4)$$

and

$$\frac{\partial \Sigma r^2}{\partial b}=2nb-2\sum y+2m\sum x=0 \qquad \ldots (5)$$

Dividing both equations by 2 we have

$$m\sum_n x^2-\sum_n xy+b\sum_n x=0 \qquad \ldots (6)$$

$$nb-\sum_n y+m\sum_n x=0 \qquad \ldots (7)$$

These equations may be solved simultaneously for m and b.

The same procedure may be followed for equations of higher order. Each increase of one in order simply requires one more parameter with respect to which Σr^2 must be minimized, and therefore increases by one the number of simultaneous equations, to be solved.

Several other important statistical values can be obtained from the squares method. The correlation coefficient gives an estimate of how well the data correlate to the straight line defined by the least squares method.

Slide Rule

The slide rule cannot be regarded as modern invention in the strict sense, as the first design dates from the early part of the seventeenth century. The underlying principle of slide a rule is calculation by logarithms. Component parts of the slide rule are shown in Fig. 18.1.

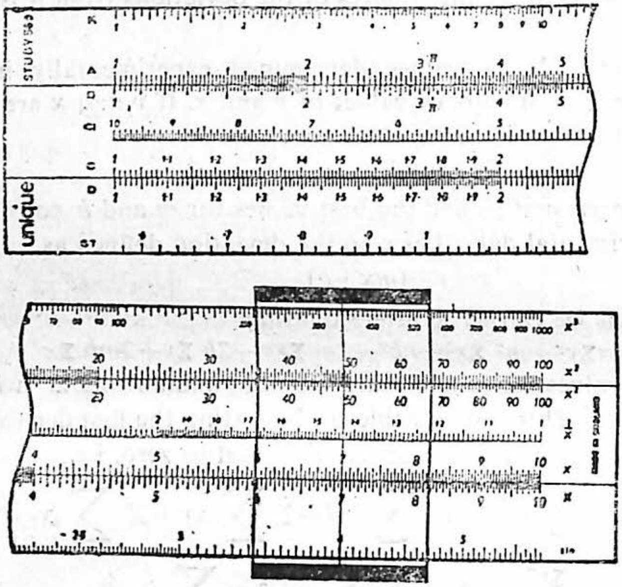


Fig. 18.1. Slide Rule.

The body of the rule is usually termed the "stock". The smaller part, which can be moved to right or left, is called the "slide" and the movable index is known as "cursor" or indicator. If you examine the stock you will find it is built up of several parts which give it a degree of flexibility.

C and D scales. There are several scales on the rule. In a general-purpose type slide rule, among others, there are two scales usually denoted by the letters *C* and *D*. Scale *C* lies along the bottom edge of the slide, and scale *D* is on the stock adjacent to the scale *C*. The two scales are identical in their graduations and are, in fact, one single scale which has been cut through lengthwise. The main graduations of scales *C* and *D* are numbered 1, 2, 3, etc. up to 10. Subdivision should be numbered as fully as possible without carrying the process to the extent of causing confusion.

A and B scales. These scales lie adjacent to one another, *A* on the stock and *B* on the upper edge of the slide. The numbering of the main divisions of scales *A* and *B*, starting from the left-hand should be 1, 2, 3, etc. up to 10, then 20, 30 etc. up to 100. The Fig. 10 marks the line midway along the length of the scale.

Scales *A* and *B* in conjunction with scales *C* and *D* give a quick means of extracting square and cube roots, and of squaring and cubing numbers. Since scale *D* is twice the length of each of the identical halves of scale *A*, it follows that as we move along scale *A*, we pass the logarithmic milestones twice as fast as when moving along scale *D*.

Log-log scales. These scales when present in a slide rule are often placed along the top and bottom edges of the stock. Log-log scales are very useful in dealing with technical problems. These are marked *LU* and *LL*.

Log scale. It is on the reverse side of the slide and is usually marked *L*. This enables us in conjunction with scale *D* to read off logarithms of numbers.

Reciprocal scale. It lies along the middle of the slide. It is divided in the same way as the *C* and *D* scales, but it is reversed and reads backward from right to left. Square roots can be conveniently obtained with the help of this scale.

Sine and tangent scales. The scale marked *S* is scale of sines. Its graduation will probably start at a value of 35 minutes and finish at 90°. This scale is used in conjunction with scale *A*.

The tangent scale is labelled *T* and the graduations start just below 6° and go up to 45°. It is used in conjunction with the *D* scale. In addition, there may be some linear scales fitted to the slide rule. These have no connection with the rule as a calculating device. They add to the appearance of the slide rule. A slide rule should be always handled carefully and must not be used for ruling lines or to take measurements, when a plastic ruler may be used.

Problem 18.1. Using the least square method; calculate the slope and intercept of the equation

$$\log K = \rho\sigma + \log K$$

if the experimental values of σ and $\log K$ are as follows:

log K	σ
4.49	1.01
6.02	2.00
7.47	2.98
9.10	4.05

Solution. First complete the table

logK	*logK*	σ	σ_3
4.49	4.54	1.01	1.02
6.02	14.04	2.00	4.00
7.47	22.26	2.98	8.88
9.10	36.86	4.05	16.40
27.08	75.90	10.04	30.30

$$q=\Sigma(\sigma)\ (\log\ K)-\frac{(\Sigma \log K)(\sigma)}{n}$$

$$= 75.70-\frac{(27.09)\times(10.94)}{4}$$

$$=7.70$$

$$Z=\Sigma\sigma^2-\frac{(\Sigma\sigma^2)}{n}$$

$$= 30\ 30-\frac{(10.04)^2}{4}$$

$$=5.10$$

$$\frac{q}{Z}=\frac{7.70}{5.10}$$

$$=1.51$$

Intercept (c)=$\log \bar{K}-P\bar{\sigma}$

$$=\frac{27.08}{4}-1.51\ \frac{(10.04)}{4}$$

$$=2.98.$$

Problem 18.2. Solve $\dfrac{8.2\times14\times7\times29.1\times77.6\times50.2}{18.6\times32.7\times1.606\times480}$

Solution. Set X to 82 D, 186 C to X, X to 147 C, 327 C to X, X to 291 C, 606 C to X, X to 776 C, 480C to X, X to 502 C.

Read the result 772 in D under X.

Approximation gives 70; the result is 77.2.

Problem 18.3. Find the tenth power of 21.

Solution. 21 lies in *LL*, but 2.1 is in *LU*, and we can use 2.1×10 and raise each factor to the tenth power. Projecting 2.1 from *LU* to *LL* we obtain 1670. The result therefore will be 1.67×10^{13}:

Problem 18.4. Using logarithm solve the following

$$y=\frac{19.86\times(98.37)^3}{\sqrt[5]{858.7}}$$

Solution. Take logarithm of both sides of this equation,

$$\log\ y=\log 10.86+3\ \log\ (98.37)-\tfrac{1}{5}\ \log 858.7$$

$$=1.036+3(1.9927)-\tfrac{1}{5}\ (2.9339)$$

$$\log y = 1.0367 + 5.7771 - 0.5868$$
$$\log y = 5.2270$$
$$y = 1.686 \times 10^5$$
$$y = 168.600.$$

EXERCISES

18.1 Write the following as power of ten:

(*a*) 0.01 (*d*) 45684.45

(*b*) 0.00245 (*e*) 0.95

(*c*) $\frac{1}{(100)^2}$

18.2. How many significant figures are indicated in each number below?

(*a*) 0.0491 (*d*) 2.3×10^7

(*b*) 3.0675×10^3 (*e*) 35×10^5.

(*c*) 23,000,000

[Ans. (*a*) 3, (*b*) 5, (*c*) 2, (*d*) 2, (*e*) 3.]

18.3. Solve the following:

(*a*) $(2.30 \times 10^7)(1.65 \times 10^{-3})$ (*d*) $(0.000212) \times (0.000063)$

(*b*) $\frac{7.81 \times 10^{-3}}{6.4298 \times 10^6}$ (*e*) $(6.9273 \times 10^2) \times (8.96 \times 10^{-3}) \times (5 \times 10^6)$

(*c*) $\frac{0.000063}{0.0000212}$

[Ans. (*a*) 3.80×10^4, (*b*) 1.215×10^{-9}, (*c*) 3.0×10^{-1}, (*d*) 1.34×10^{-8}, (*e*) 3×10^7.]

18.4. How many significant figures are there in each of the following numbers, assuming that there is uncertainty of ±1 unit in the last digit?

(*a*) 3.07, (*b*) 307, (*c*) 0.00307, (*d*) 3.070×10^{-3}.] Ans. (*a*)]

18.5. Using your slide rule, find the square root of (*i*) 22.2, (*ii*) 15.2, (*iii*) 30.0. [Ans. (*i*) 4.71, (*ii*) 3.90, (*iii*) 54.7.]

18.6. Using your slide rule find the value for (*i*) $(2.3)^2$, (*ii*) $(43.0)^2$, (*iii*) $(0.0810)^2$. [Ans. (*i*) 5.3, (*ii*) 1.85×10^3, (*iii*) 6.56×10^{-3}.]

18.7. Using your slide rule find the cube root of 2.3×10^{-4}. [Ans. 6.13×10^{-2}.]

18.8. Given the exponential equation $a^x \cdot a^y = a^z$, write z in terms of x and y. [Ans. $z = x + y$.]

18.9. Given the exponential equation $(m^r)^s = m^t$, write t in terms of r and s. [Ans. $t = r \cdot s$.]

18.10. Write the answers to the following in the simple exponential form:

(*a*) $\frac{U^3 \times 10^5}{U^4 \times 10^7}$, (*b*) $\frac{4.10^5}{u \cdot 10^{-6}}$, (*c*) $p^0 \cdot q^3$.

$\left[\text{Ans. } (a)\ U^{-1} \cdot 10^{-2},\ (b)\ \frac{4}{\pi} \cdot 10^{11},\ (c)\ q^3.\right]$

18.11. Write each of the following as a single exponential:

(*a*) $\sqrt[3]{8}$, (*b*) $\sqrt[5]{P}$, (*c*) $\sqrt{10}$.

[Ans. (*a*) $8^{\frac{1}{3}}$, (*b*) $P^{\frac{1}{5}}$, (*c*) $10^{\frac{1}{2}}$.]

18.12. What is the logarithm of

(*a*) 2.55, (*b*) 890, (*c*) −0.0067.

[Ans. (*a*) 0.407, (*b*) 2.949, (*c*) 0.826−3.]

18.13. What is the antilogarithm of

(*a*) 0.548, (*b*) 2.708, (*c*) −2.687.

[Ans. (*a*) 3.53, (*b*) 5.10×10^2, (*c*) 0.00206.]

18.14. Solve the following using logarithms:

(*a*) $6.67 \times 10^{-27} \times 1.38 \times 10^{18}$, (*b*) $6.02 \times 10^{-23} \div 4.80 \times 10^{-30}$, (*c*) $(4.60)^{1/5}$.

[Ans. (*a*) 9.20×10^{-9}, (*b*) 1.25×10^7, (*c*) 1.36.]

18.15. What is the antilog$_3$ (to the base 3) of the following numbers:

(*a*) 3.0, (*b*) 2.0, (*c*) 0.5.

[Ans. (*a*) 27, (*b*) 9, (*c*) 1.732.]

APPENDIX I

GREEK CHARACTERS

α	alpha
β	beta
γ	gamma
δ	delta
ε	epsilon
ζ	zeta
η	eta
θ	theta
$\varkappa$	kappa
λ	lambda
μ	mu
ν	nu
$\bar{\nu}$	nu-bar
π	pi
ρ	rho
σ	sigma
τ	tau
ϕ	phi
χ	chi
ψ	psi
ω	omega
∇	delta

APPENDIX II

METRIC MULTIPLES

	Prefix	*symbol*
10^9	Giga	G
10^6	Mega	M
10^3	Kilo	k
10^{-1}	Deci	d
10^{-2}	Centi	c
10^{-3}	Milli	m
10^{-6}	Micro	μ
10^{-9}	Nano	n
10^{-12}	Pico	p

APPENDIX III

SI UNITS AND SOME PHYSICAL CONSTANTS

These days there is tendency to adopt international system of units referred to as SI (Systeme International d'Unites). This is based on the following seven independent physical quantities given in Table I.

TABLE I. SI units and unit symbol for some physical quantities

Physical quantity	*Basic SI unit*	*Unit symbol*
Length	metre	m
Mass	kilogramme	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mole
Luminous intensity	candela	cd

TABLE II. SI units for some of the physical quantities

Physical quantity	*SI unit*
Area, A	m^2
Volume, V	m^3
Pressure, P	Nm^{-2} Jm^{-3}
Molar volume, V_m	m^3 $mole^{-1}$
Work	J
Heat	J
Enthalpy	J
Helmholtz free energy, A	J
Gibbs free energy, G	J
Entropy, S	JK^{-1}
Heat capacity	JK^{-1}
Molar gas constant, R	JK^{-1} $mole^{-1}$
Boltzmann constant, k	JK^{-1}

Partial molar volume of a substance B, V_B	$m^3\ mole^{-1}$
Osmotic pressure, π	Nm^{-2}
Polarizability of a molecule, α	$Cm^2\ V^{-1}$
Dipole moment of a molecule, μ	Cm
Faraday constant, F	$C\ mole^{-1}$
Electric conductance	Ω^{-1}
Specific conductance, K	$\Omega^{-1}\ m^{-1}$
Molar conductance μ	$\Omega^{-1}\ m^2\ mole^{-1}$
Transport number of an ion, tt	Dimensionless
Activation energy ΔE	$J\ mole^{-1}$
Collision number, Z	$m^{-3}\ s^{-1}$
Planck's constant, h	Js
Wavelength, λ	m

However some non-SI units, such as minute, hour, degree, celsius and litre are also in use.

TABLE III. Values for some physical constants

Quantity	*Symbol*	*Value SI units*
Speed of light	c	$2.997925 \times 10^8\ ms^{-1}$
Planck constant	h	6.62620×10^{-34} Js
Avogadro number	N	$6.02217 \times 10^{23}\ mole^{-1}$
Electron charge	$-e$	1.602192×10^{-19} c
Electron rest mass	m_e	9.10956×10^{-31} kg
Proton rest mass	m_e	1.67261×10^{-27} kg
Faraday constant	F	$9.64867 \times 10^4\ C\ mole^{-1}$
Bohr magneton	μ_B	$5.05096 \times 10^{-27}\ JT^{-1}$
Rydberg constant	R_H	$1.0973731 \times 10^7\ m^{-1}$
Bohr radius	a_0	5.291772×10^{27} m
Nuclear magneton	μ_N	$5.05095 \times 10^{-27}\ JT^{-1}$
Boltzmann constant	k	$1.38062 \times 10^{-23}\ J.K.^{-1}$
Gas constant	R	$8.3143 \times JK^{-1}\ mole^{-1}$

APPENDIX IV

COMMON DERIVATIVES AND INTEGRALS

Consider two functions u and v, which are functions of x only and a is a constant.

Derivatives

$$\frac{d(a)}{dx}=0 \qquad \frac{d(au)}{dx}=a\frac{du}{dx}$$

$$\frac{d(x^n)}{dx}\,nx^{n-1} \qquad \frac{d(u^n)}{dx}\;nu^{n-1}\frac{du}{dx}$$

$$\frac{d(e^x)}{dx}=e^x \qquad \frac{d(e^v)}{dx}=e^v\frac{dv}{dx}$$

$$\frac{d(a^x)}{dx}=a^x\ln a \qquad \frac{d(\ln x)}{dx}=\frac{1}{x}$$

$$\frac{d(a^u)}{dx}=a^u\ln a\frac{du}{dx} \qquad \frac{d\log_{10}x}{d\,x}=\frac{1}{2.3026\,x}$$

$$\frac{d\ln u}{dx}=\frac{1}{u}\frac{du}{dx} \qquad \frac{d\log u}{dx}=\frac{1}{2.3026\,u}\frac{dx}{dx}$$

$$\frac{d(u+v)}{dx}=\frac{du}{dx}+\frac{dv}{dx}$$

$$\frac{d(uv)}{dx}=u\frac{dv}{dx}+v\frac{du}{dx}$$

$$\frac{d(u/v)}{dx}=\frac{1}{v}\frac{du}{dx}-\frac{u}{v^2}\frac{dv}{dx}$$

$$\frac{d(\sin x)}{dx}=\cos x \qquad \frac{d(\sin u)}{dx}=\cos u\frac{du}{dx}$$

$$\frac{d(\cos x)}{dx}=-\sin x \qquad \frac{d(\cos u)}{dx}=-\sin u\frac{du}{dx}$$

Integrals

$$\int dx=x+C \qquad \int x^n dx=\frac{x^{n+1}}{n+1}+C\ (n\neq 1)$$

$$\int\frac{dx}{x}=\ln x+C \qquad \int e^x dx=e^x+C$$

$$\int a^x dx=\frac{a^x}{\ln a}+C \qquad \int \ln x\,dx=x\ln x-x+C$$

$$\int \sin x\,dx = -\cos x + C$$

$$\int \cos x\,dx = \sin x + C$$

$$\int (ax+b)^n\ dx = \frac{(ax+b)^{n+1}}{a(n+1)} + C\ (n \neq 1)$$

$$\int \frac{dx}{ax+b} = \frac{ln\ (ax+b)}{a} + C$$

$$\int \frac{x dx}{ax+b} = \frac{x}{a} - \frac{b}{a^2} ln\ (ax+b) + C$$

$$\int \frac{x^2 dx}{ax+b} = \frac{1}{a^3}\left[\frac{(ax+b)^2}{2} - 2b\ (ax+b) + b^2\ ln\ (ax+b)\right] + C$$

$$\int au dx = a \int u dx$$

$$\int (u+v) dx = \int u dx + \int v dx$$

$$\int u dv = uv - \int v du$$

$$\int e^{ax} x^n dx = \frac{n!\ e^{ax}}{a^n+1}\left[\frac{(ax)^n}{n!} - \frac{(ax)^{n-1}}{(n-1)!} + \frac{(ax)^{n-2}}{n-2)!} + (-1)^r \frac{(ax)^{n-r}}{(n+r)!} + \right.$$

$$\left. \ldots + (-1)^n \right] + C$$

$$\int_0^\infty e^{-ax^2} dx = \tfrac{1}{2}\sqrt{\frac{\pi}{a}} \qquad \int_0^\infty e^{-ax^2}\ x dx = \frac{1}{2a}$$

$$\int_0^\infty e^{-ax^2}\ dx = \tfrac{1}{4}\sqrt{\frac{\pi}{a^3}} \qquad \int_0^\infty e^{-ax^2}\ x^3 dx = \frac{1}{2a^2}$$

The general formula of the integral for even values of n is

$$\int_0^\infty e^{-ax^2}\ x dx = 1.3.5\ldots(n-1)\,\frac{(\pi a)^{\frac{1}{2}}}{(2a)^{\frac{1}{2}(n+1)}}$$

for odd values of n

$$\int_0^\infty e^{-ax^2} x^n\ dx = \frac{\left[\frac{1}{2(n-2)}\right]!}{2a^{[\frac{1}{2}](n+1)}}$$

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
10	0000	0043	0086	0128	0170						5 9 13	17 21 26	30 34 38
						0212	0253	0294	0334	0374	4 8 12	16 20 24	28 32 36
11	0414	0453	0492	0531	0569						4 8 12	16 20 23	27 31 35
						0607	0645	0682	0719	0755	4 7 11	15 18 22	26 29 33
12	0792	0828	0864	0899	0934						3 7 11	14 18 21	25 28 32
						0969	1004	1038	1072	1106	3 7 10	14 17 20	24 27 31
13	1139	1173	1206	1239	1271						3 6 10	13 16 19	23 26 29
						1303	1335	1367	1399	1430	3 7 10	13 16 19	22 25 29
14	1461	1492	1523	1553	1584						3 6 9	12 15 19	22 25 28
						1614	1644	1673	1703	1732	3 6 9	12 14 17	20 23 26
15	1761	1790	1818	1847	1875						3 6 9	11 14 17	20 23 26
						1903	1931	1959	1987	2014	3 6 8	11 14 17	19 22 25
16	2041	2068	2095	2122	2148						3 6 8	11 14 16	19 22 24
						2175	2201	2227	2253	2279	3 5 8	10 13 16	18 21 23
17	2304	2330	2355	2380	2405						3 5 8	10 13 15	18 20 23
						2430	2455	2480	2504	2529	3 5 8	10 12 15	17 20 22
18	2553	2577	2601	2625	2648						2 5 7	9 12 14	17 19 21
						2672	2695	2718	2742	2765	2 4 7	9 11 14	16 18 21
19	2788	2810	2833	2856	2878						2 4 7	9 11 13	16 18 20
						2900	2923	2945	2967	2989	2 4 6	8 11 13	15 17 19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 15 17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 3 5	7 9 10	12 14 15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 13 14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 8 9	11 12 14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 6 8	9 10 12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 3 4	5 6 8	9 10 11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1 2 4	5 6 7	8 10 11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1 2 3	5 6 7	8 9 10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1 2 3	5 6 7	8 9 10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1 2 3	4 5 7	8 9 10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1 2 3	4 5 6	8 9 10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1 2 3	4 5 6	7 8 9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1 2 3	4 5 6	7 8 9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1 2 3	4 5 6	7 8 9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1 2 3	4 5 6	7 8 9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1 2 3	4 5 6	7 8 9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1 2 3	4 5 6	7 7 8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1 2 3	4 5 5	6 7 8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1 2 3	4 4 5	6 7 8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1 2 3	4 4 5	6 7 8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	123	456	789
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1 2 3	3 4 5	6 7 8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1 2 3	3 4 5	6 7 8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 3	3 4 5	6 7 7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1 2 2	3 4 5	5 6 7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 2 2	3 4 5	5 6 7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 1 2	3 4 4	5 6 7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1 1 2	3 4 4	5 6 6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2	3 4 4	5 6 6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2	3 3 4	5 6 6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2	3 3 4	5 5 6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2	3 3 4	5 5 6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 3 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 3 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 3 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 3 4	4 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	2 3 4	4 5 6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2	2 3 4	4 5 6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1 1 2	2 3 4	4 5 5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	2 3 4	4 5 5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1 1 2	2 3 3	4 5 5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2	2 3 3	4 4 5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2	2 3 3	4 4 5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0 1 1	2 2 3	3 4 4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1	2 2 3	3 4 4
89	9494	9499	9504	9509	9515	9318	9523	9528	9533	9538	0 1 1	2 2 3	3 4 4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
95	9777	9782	9736	9791	9795	9800	9805	9809	9814	9818	0 1 1	2 2 3	3 4 4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0 1 1	2 2 3	3 4 4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 4 4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0 1 1	2 2 3	3 3 4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0 0 1	1 1 1	2 2 2
01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0 0 1	1 1 1	2 2 2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0 0 1	1 1 1	2 2 2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0 0 1	1 1 1	2 2 2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0 1 1	1 1 2	2 2 2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0 1 1	1 1 2	2 2 2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0 1 1	1 1 2	2 2 2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0 1 1	1 1 2	2 2 2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0 1 1	1 1 2	2 2 3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0 1 1	1 1 2	2 2 3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0 1 1	1 1 2	2 2 3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0 1 1	1 2 2	2 2 3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0 1 1	1 2 2	2 2 3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0 1 1	1 2 2	2 3 3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0 1 1	1 2 2	2 3 3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0 1 1	1 2 2	2 3 3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0 1 1	1 2 2	2 3 3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0 1 1	1 2 2	2 3 3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0 1 1	1 2 2	2 3 3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0 1 1	1 2 2	3 3 3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0 1 1	1 2 2	3 3 3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0 1 1	2 2 2	3 3 3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0 1 1	2 2 2	3 3 3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0 1 1	2 2 2	3 3 4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0 1 1	2 2 2	3 3 4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0 1 1	2 2 2	3 3 4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0 1 1	2 2 3	3 3 4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0 1 1	2 2 3	3 3 4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0 1 1	2 2 3	3 4 4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0 1 1	2 2 3	3 4 4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0 1 1	2 2 3	3 4 4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0 1 1	2 2 3	3 4 4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0 1 1	2 2 3	3 4 4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0 1 1	2 2 3	3 4 4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1 1 2	2 3 3	4 4 5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1 1 2	2 3 3	4 4 5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1 1 2	2 3 3	4 4 5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1 1 2	2 3 3	4 4 5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1 1 2	2 3 3	4 4 5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1 1 2	2 3 3	4 5 5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1 1 2	2 3 4	4 5 5
41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1 1 2	2 3 4	4 5 5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1 1 2	2 3 4	4 5 6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1 1 2	3 3 4	4 5 6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1 1 2	3 3 4	4 5 6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1 1 2	3 3 4	5 5 6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1 1 2	3 3 4	5 5 6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1 1 2	3 3 4	5 5 6
48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1 1 2	3 4 4	5 6 6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1 1 2	3 4 4	5 6 6

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
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